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MODERN THEORIES

OF

CHEMISTRY

BY

DR LOTHAR MEYER

PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF TÜBINGEN

TRANSLATED FROM THE GERMAN (5TH EDITION)

BY

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TRANSLATORS' PREFACE.

In undertaking this translation we have been actuated by a desire to make Lothar Meyer's 'Moderne Theorien der Chemie' as accessible to the English student of chemistry as it is to his contemporary in Germany. The original has already passed through four editions; and if testimony were needed as to the esteem in which this book is held, it can surely be found in the fact that no sooner had the fourth edition been completed than a fifth was demanded.

The character of the work is such that we felt convinced that duty demanded we should make our translation as far as possible a reproduction of the original, and with this conviction we have throughout adhered closely to the text.

Our original intention had been to publish a translation of the fourth edition, and the greater portion of the work had already been completed when the appearance of the fifth edition required a revision of the first two parts and a retranslation of the third. These facts, together with other circumstances, have combined to delay the publication.

The scope of the work is sufficiently explained in the Author's Preface to the Fourth Edition, a translation of which will be found on p. vii. We have not deemed it necessary to publish also the brief preface to the fifth, in which the author has simply stated the conditions which led to the rapid succession of these editions, and has noted the points in which the fifth differs from its immediate predecessor. These are as

follows: in the first part the use of the atomic weights recalculated by the author and Dr. Seubert; the second part has been shortened to some extent; and in the third part considerable changes have been made, especially in those portions relating to the thermal phenomena accompanying chemical changes, and also in the chapters devoted to the action of mass.

During the passage of the book through the press we have been able to make a few additions, such as the determination of the vapour density of potassium iodide by Victor Meyer, the result of which has been introduced into the table of vapour densities and molecular weights, p. 42. The interesting results of the investigations of V. Meyer and J. Mensching (*Ber. d. deut. chem. Ges.*, xx. 1833) on the behaviour of phosphorus, arsenic, and antimony at a white heat have been published so recently as to make it impossible to include them in the table on p. 28. A short statement of these results is, however, to be found amongst the addenda, where will also be found some account of the determinations of the physical constants of Germanium and of its compounds.

In conclusion we would express our gratitude to Mr. Saville Shaw and others for the aid so kindly given in revising the sheets for the press.

THE TRANSLATORS.

October 1887.

AUTHOR'S PREFACE

TO THE FOURTH EDITION.

When, in the year 1862, I undertook this work, it was with the desire and hope that its publication might contribute to the removal of the doubts and uncertainties, so frequently expressed at that time, as to the character of the views and theories then contending for supremacy in chemistry. It was my firm conviction that the confusion in the discussions of that time chiefly arose from erroneous views as to the importance of hypotheses and theories, upon which some were inclined to place too high a value, whilst others again did not sufficiently recognise their true importance. The chief aim of my undertaking was to show that hypotheses and the theories based upon them are necessary aids to chemical investigation, and at the same time to assign to them their true value and place them in a position similar to that which they occupy in theoretical physics. In this way I had hoped to prepare the way for the further development of theoretical chemistry, and at the same time to make the more recent results accessible to wider circles; but when, two years later, after having for the third time revised the manuscript, it was handed to the printer, I felt that the work would possibly be of service to those men of science who had not specially devoted themselves to chemistry, but I seriously doubted whether

it might prove useful to chemistry or its representatives. Being fully aware that a work dealing with theoretical matters alone was in direct opposition to the prevailing custom, which permitted only a few careful speculations and theoretical considerations to be mentioned in connection with the results of experimental investigation, and although no pains had been spared, I yet entertained grave doubts as to whether the result was such that my colleagues would be ready to extend due consideration to one who had thus shown so little regard for the accepted custom. Furthermore, the book appeared to me not sufficiently thorough, but ill-supplied with positive contents, so much so that I abandoned my original idea of dedicating it to my honoured teacher.

The manner in which this book has been received amongst chemists of every section and party has satisfied me that my doubts arose to a large extent from anxiety. I had been frequently assured that an account by an impartial critic, and a careful selection of the various theories which had either ruled or striven for rule at different periods in the history of chemistry, would exactly meet the requirements of chemists at that time, and, therefore, prove acceptable to them. I am not in a position to judge whether in what I have done my object has been fully realised.

The aim of the first edition was an ephemeral one, as I had attempted therein to clear away the doubts and uncertainties surrounding the views held by chemists, and at the same time to give to others interested in the science an account such as would lead to an understanding of the change through which the system of chemistry has just passed. The character of the book was naturally determined by the aim; it appeared doubtful whether at any future time a second edition would be required, or even whether it would be advisable to publish one. But, as there was still a demand for the book in its first form, although the edition had been for many years exhausted, I consented, in compliance with the wishes expressed

by the publishers, to the appearance of the second and third editions.

To make the present edition more suited to the requirements of the time, a complete revision and rewriting of much has been necessary, and in it I have on the one hand attempted to give an account of the latest developments of chemical theories, and on the other have, by the introduction of the more important empirical data, sought to make the theoretical conclusions arrived at by their aid easier to follow and the causes leading to their foundation clearer. The book has, therefore, assumed more the character of a text- or hand-book; to make it one entirely of this description did not appear to me, at any rate for the present, advisable. To add to its value as a handbook and book of reference I have divided it into distinct sections, a plan which was not adopted in the first edition, excepting so far as to separate the introduction and conclusion from the rest of the book. The number of the sections in this edition has been almost doubled, and these are grouped into three books, the first dealing with atoms and their properties, the second with the Statics of the atoms, or the doctrine of the equilibrium of the atoms in their combinations with one another, and the third with the dynamics of the atoms or the doctrine of chemical change. This mode of subdivision has necessitated transferring the ninth section of the work to the first book, as Section V. In consequence of this and other changes the numbers attached to the paragraphs, from § 34 on, have been altered. To aid in referring to previous editions, the numbers representing the paragraphs of the third edition have been allowed to remain, where the contents of the paragraphs have remained practically unaltered: these numbers are enclosed in brackets; new paragraphs have only one number attached.

This work was originally published under the title 'The Modern Theories of Chemistry,' which has been retained for the successive editions, despite the fact that doubts have been

expressed as to its suitability. It is scarcely necessary for me to explain that I considered the title not as a matter of fashion, but used the expression 'modern' in contradistinction to 'antique' or 'old,' as is usual in the history of Art and of Science. Such a distinction existed without doubt at the time of the publication of the first edition, a distinction as sharply defined as that existing between ancient and modern Art and Culture. Although I may still believe that the title was not unsuitably chosen, yet I do not in the least agree with the use of the term '*modern*' when referring to '*chemistry*,' but only as I have used it in reference to the '*theories*'; for in my opinion no change has been effected in chemistry in the last hundred years, with perhaps the single exception of the passage from the phlogistic to the antiphlogistic system, which has been of so revolutionary a character as to justify a line of demarcation between an old and a new or modern chemistry. The transition from the dualistic to the unitary system, despite the numerous alterations it entailed, does not certainly justify such a separation; for the most essential scientific results and the methods of investigation have remained unaltered, or have gradually and steadily developed. The fact that some of the old hypothetical views are now discarded, whilst others meet with general recognition, can scarcely be regarded as forming sufficient ground for speaking of the chemistry of to-day as a modern science, as opposed to that which was taught in the first half of this century; whilst at all events between the theories accepted at the present time and those of the same period such a sharply defined distinction certainly does exist. I intended on a former occasion to draw attention to this, in my opinion, unjustifiable transference of the term modern from the theories to chemistry itself, but have not done so, as I found that a similar application had already been made at the period of transition from the phlogistic to the antiphlogistic system. Lavoisier's antiphlogistic views were

published under the title 'Traité Elémentaire de Chimie présentée dans un ordre nouveau et d'après les découvertes modernes,' whilst a few years later Fourcroy gave to his work the title 'Philosophie Chimique, ou Vérités Fondamentales de la Chimie Moderne.' Both methods of using the word 'modern' have, therefore, a certain historical justification, which is all the more deserving of attention as a certain similarity between the conditions at the end of the fifth and the beginning of the sixth decade of this century and those prevailing at the end of the last century is not to be overlooked.[1]

In this, as in former editions, the most important references to the literature are given, with a view to aid in a more comprehensive study of the subject. In this edition a certain amount of restriction has been necessary, as it is impossible to cite in every case all the workers who have been successfully engaged in a particular subject. References are not given where the empirical data can be obtained from text- or hand-books, or from the 'Jahresberichte,' but when the information is not so easily attainable the sources are given as completely as possible. I have done my utmost to trace theoretical deductions to their true originator, without attempting in every case to state where and when they were first published. In the case of the introduction of general rules and leading principles into the science, I have considered it necessary to mention only those authors who were either the first to enunciate such principles or to have extended them, or first clearly indicated their import, and have thought it unnecessary, as it is almost impossible, to cite each of those who have applied such general rules. Thus, for example, mention has been made of the works which have been of special service in establishing the validity of the general principles upon

[1] *Die Entwickelung der modernen Chemie*, Braunschweig, 1879, p. 34. Herr Albrecht Rau has in an inconceivable manner misunderstood these remarks, which appeared in the preface to the second edition of this book, and would have it believed that I had sought to make a comparison between an individual from among the 'men of modern chemistry' with Lavoisier.

which the determination of the atomic weights are based, but I have not cited all the investigations, however valuable they may be, which have contributed to the recognition of the utility of these rules and their application in the case of certain elements. In like manner I have scarcely deemed it necessary, save in a few special cases, to mention when each single application of the law of atomic linking was first made. It is scarcely possible to attain to completeness in references of this kind, and absolute certainty could only be arrived at by the expenditure of time and trouble altogether out of proportion to the result. I may be allowed to express the hope that I have, on the whole, succeeded in assigning the right proportion to each section, though from the very first I doubted whether my colleagues would agree with me in the amount of space devoted to the section dealing with the forms of combination and the linking of the atoms; in fact, the suggestion has been made that I have paid too little attention to the part taken by some investigators in the development of the theories relating to the constitution of organic compounds.

My reply to this suggestion is that it was never my intention to write a history of organic chemistry, but simply to sketch the development of certain well-defined theories, which after long-continued opposition at last have obtained general recognition. The origin and the development of the majority of the theories dealt with—e.g. Dalton's atomic theory, Avogadro's hypothesis, Dulong and Petit's law—are easily grasped and can be presented historically in a few short sentences. This is by no means the case with the development of the type system and of the theory of atom-linking, neither of which has been the result of a special series of observations, nor could either have at once attained its present completeness. They are rather the slowly-matured fruit of much experimental investigation than of theoretical speculation. Their growth and development is not more

the result of the investigations and arguments of their founders than of the conditional and unconditional opposition of their opponents, so that every chemist who has taken part in the advance of chemistry, especially of organic chemistry, has contributed, directly or indirectly, to the development of these theories. Although this fact has not been passed over in the text, it is neither expressly stated nor is it evident from the references given.

To make the representations perfectly clear, not only would considerable additions be required to the already large stock of experimental data, but it would also necessitate more lengthy discussions, and such discussions themselves would involve special difficulties from the different positions assumed by individual chemists toward theoretical speculations. Many of those observers whose work has opened up quite new provinces, by which theoretical chemistry has largely benefited, have preferred either to suppress the speculations upon which their investigations were based, or, only touching lightly upon these, to leave the reader to draw the theoretical conclusions to be deduced from the new discoveries. Again, the conclusions of many are set forth in expressions and formulæ to which special meanings were attached, and which to-day are only to be interpreted with great difficulty and labour. In fact, for a long time chemical terminology was in a state of confusion, the same word being frequently employed by different parties with exactly opposite meanings. This would necessitate, therefore, a thorough discussion of the mode of expression of the various times and systems and a translation of this language into that of the present day. Further, opposition has arisen and disappeared not only in literary polemics, but has frequently been the result of mere personal exchange of opinion. All these conditions combine to make a complete and true representation of the history of the development of the theory of atomic linking, despite its attraction, an extremely difficult task, and one which, although

not impossible in the present generation, still would require more time and space than are at my disposal. With these considerations, therefore, I have, although unwillingly, relinquished the attempt to give an account of this history, and in the sketch thereof have, as in the first edition, mentioned only those investigators from whom the theory obtained a fixed and definite form, others being mentioned only when examples have been taken from their works.

The most important changes in this edition arise from the introduction of a third book dealing with the dynamics of the atoms, thus completing chemical mechanics. I have been led to make this addition despite the fact that I still hold to some extent the views expressed in the preface to the second edition as to the unripeness of this portion of the science, a condition which has made it difficult to decide upon its introduction into my book. But, as it appeared to me that sufficient reliable data were to be found to enable me to give an outline which at some future time, by the introduction of the results of further investigations, would form a complete edifice, I have not refrained from attempting the difficult but at the same time interesting task. In carrying out the enterprise I certainly found the work beset with greater difficulties than I ever imagined. Frequent changes have been made in the selection and arrangement of the material, and many matters which, after much consideration, I have deemed it advisable to omit, have caused as much trouble and thought as that which now forms a portion of the work. As amid the labours of the session I have not been able to obtain leisure sufficient for the collection, sifting, and elaboration of this material, and the vacation has had to serve other purposes, the publication of the third book of this work has, to the disappointment of the publishers and of myself, been greatly delayed. Had I foreseen the delay, I should have preferred publishing the first two books in one volume and making the third into a second volume. At the end of the

work are to be found notices of a few changes necessitated since the publication of the first two books.

The separate sections of the third book are very unequal in contents and extent, and this for various reasons. In those cases where the theoretical consideration of the matter has allowed it, I have contented myself with a short account of the same without introducing the various details, leaving to the reader the application of the theory to special cases. When the representation appeared to be the immediate outcome of the results of observation, I have not introduced the latter when they could be found collected together in other works, but have preferred to refer the reader to these works. This has been done in the case of thermal actions of various kinds, for which I can refer the reader to Thomsen's original work, and also the account of these phenomena given by Naumann and H. Jahn. I have not made any use of, but have entirely excluded, all matters which appeared to me not sufficiently ripe for theoretical conclusions, and amongst such belong many of the thermochemical data which, although indicating certain relationships, are despite this at the present time of value only as empirical data, which cannot with any degree of certainty be made to form the basis of theoretical conclusions. To this class of material belong also the numerous photochemical observations which, despite their practical importance and much that is remarkable and attractive in them, are not capable of theoretical handling, as are the measurements made by Bunsen and Roscoe.

In two sections only have I made considerable use of experimental data, viz. that dealing with electrolysis and that with the action of mass. Although there are works which are devoted entirely to electrolysis and allied subjects, still I have not been able to make use of these nor to refer to them, as they are as a rule, even in the case of the work of G. Wiedemann, written from the physical standpoint for physicists,

and not for chemists, where the dependence of the phenomena upon the material nature of the bodies taking part in the changes should form the chief consideration. For this reason I have been obliged to refer back to the original in the case of almost every fact made use of, in order to form a reliable judgment as to their adaptability for theoretical conclusions. I may perhaps be allowed to express the hope that this collection of the facts made for the special use of chemists may not prove unwelcome to physicists, and that the many wants it indicates, and the doubts which it gives rise to, may serve as an incentive to further investigation. On the other hand it may also serve to induce chemists to again take up the investigation of this long-neglected and important subject, joining issue with those physicists who have recently pursued it with such important results. For only by a joint application of chemical and physical methods of investigation will it be possible to obtain a clear insight into electrochemical phenomena, which are as interesting as they are important.

The section devoted to the Influence of Mass is likewise replete with experimental data, the reason being that no such collection exists of the results of investigations obtained in this department, a field of investigation too little regarded by chemists at the present time, and in which the next development of the science will doubtless be made. When, some twenty years ago, I drew attention to the necessity for continuing the investigations of Berthollet, my remarks received but little attention, for other matters then awaited solution. The beginnings of a new doctrine of affinity, which doubtless belongs to the future, are gradually being evolved from the results obtained in the study of the action of mass. The state of the science at present more nearly resembles the condition of a hundred years ago than the majority of chemists imagine. The latest development of organic chemistry, especially since the great activity in the dye and colour

industries, resembles the last stage of the phlogistic period, when new compounds of great importance were being continually discovered, but the quantitative relations between the bodies used in their preparation were considered only as they influenced the yield of the product sought. As Lavoisier introduced weight and measure into the chemistry of the phlogistians, so will the new doctrine of the action of mass determine the direction of the science in the future. The numerous reactions of organic chemistry discovered in the last decade must be quantitatively examined, their dependence on mass and temperature exactly determined; secondary reactions must be avoided, or likewise be the subject of qualitative and quantitative examinations: in short, the qualitative period of organic chemistry must be followed by one in which, as has happened in inorganic chemistry, not only the compounds but also the reactions themselves will be examined quantitatively. In order to direct the attention of my colleagues to this change of front, the most important of the material already obtained has been collected together and somewhat exhaustively treated. So soon as these results find their way into the ordinary text-books I shall be able to omit these details from a future edition, and can then devote the space to a discussion of the general theory and its limitations.

From the nature of the subject the first attempt to make a sketch of Chemical Dynamics must necessarily be very incomplete. Despite the time and trouble expended on it, I simply look upon what I have done as nothing more than an outline, and trust the reader will regard it in the same light, and judge accordingly.

TÜBINGEN, *April* 1883.

INTRODUCTION

TO

THE FIRST EDITION.

Some sixty years have elapsed since Claude Louis Berthollet published to the scientific world his classical work, 'Essai de Statique Chimique.'[1] The object of this work was to show that all the various chemical phenomena may be deduced from distinct unalterable fundamental properties of matter, just as astronomy has shown the celestial phenomena to be dependent upon the single principle of universal gravitation.

Berthollet started with the supposition that the reciprocal attraction of matter, which has been known as affinity since the infancy of the science of chemistry, is probably a phase of the same fundamental property of matter as that to which universal gravitation owes its origin. That the action of affinity appears much more complicated than that of gravity he thought might be explained by the close proximity of the substances reacting upon one another. For in this case, owing to the minute distance separating the reacting substances, the phenomena are influenced not only by the mass and distance of the smallest particles or molecules but also by their form, their distances from one another and the peculiar conditions under which they exist. To the influence of these special conditions, generally unknown to us, Berthollet

[1] Paris, 1803.

attributes our inability to deduce chemical phenomena from one general principle as is done in the case of astronomical phenomena. Although a large number of cases of the action of affinity had been investigated, still it was only possible to submit a few of these to the critical methods of calculation. Hence, chemists are compelled to observe phenomena step by step; nevertheless, it is to be expected, that as the principia deduced from such observations become more general, they will more nearly resemble the principles of mechanics. Observation alone must lead to this stage of perfection, which may now be regarded as the goal to be attained.

If we acknowledge the object of all natural science to be the explanation of the causal connection of phenomena in such a manner that the resulting phenomena can in all possible cases be predicted from the given conditions, then the object proposed by Berthollet is assuredly, for chemistry, the summit to the attainment of which all efforts must finally be directed. The object remains unchanged even if Berthollet's supposition, that gravitation and affinity are of similar origin, cannot be justified. If chemical phenomena are not to be regarded as resulting from the actions of chance, then it must be acknowledged that they are subservient to the general principles of mechanics, to the laws of equilibrium and of motion; and that 'the curve described by a single atom is as fixed as the path of a planet, and between the two cases no other difference exists save that resulting from our ignorance.'[1] Hence, the highest and final aim of all chemical investigation must be the development of chemical statics and mechanics; the doctrine of equilibrium of chemical forces and of the motion of matter under their influence. Possessed of the knowledge of the general principles of these doctrines, it will then be possible to predict from given conditions, the result of

[1] Laplace, *Essai philosophique sur les probabilités*: 3me éd. Paris, 1816, p. 6.

their action in any particular case. Thus the science will have attained the state of perfection which Berthollet had in view.

For the attainment of this object it is necessary, first to solve the converse problem, viz. to discover and measure those quantities which, in the various phases of each phenomenon, remain unaltered under all circumstances. Further, to discover the laws expressing the dependency of the phenomenon on these constants and on external conditions. Hence Berthollet's demand that phenomena should be followed step by step, for a general theory cannot be elaborated until a large and specially chosen number of phenomena have been empirically and logically analysed. From the thorough study of the phenomena and of the conditions under which they take place, and aided by the general ideas so obtained, it is, as a rule, a comparatively easy task to predict single phenomena with or without the aid of mathematics.

A review of the development of chemistry since Berthollet's time shows that at any rate a wide range of material has been submitted to investigation, and an extraordinarily large number of facts added to our knowledge. It cannot, however, fail to be noted that but a small proportion of these have been so thoroughly studied as to allow the influence of every single important condition to be systematically followed, and thus render evident the causal connection of the phenomena. But little advance has been made in the direction which Berthollet had in view. Chemical statics appears still to stand in the position to which this gifted thinker had led it. His great work stands in the midst of our immensely extended literature, like a lost landmark, to many perhaps unknown, studied by the few, completed and perfected by none.

But no just reproach can be brought against chemists on these grounds. That, of the many famous men who have dedicated their whole strength to chemistry, but few only have

endeavoured to follow in the direction indicated by Berthollet, whilst the majority have forsaken the path and have sought to extend the science in totally distinct directions, shows to the impartial critic, that this course of action arose from an indispensable necessity for the development of the science in other directions. The more recent history of chemistry affords a complete justification of this view. For a little consideration will show that only by taking a direction exactly opposed to that proposed by Berthollet could chemistry gain the rank of an independent science, a position to which it has scarcely yet attained.

That the brilliant ideas of Berthollet have exercised relatively so slight an influence on the progress of chemistry can be to a great extent explained by the fact, that Berthollet believed he was nearer the stage of development which he desired to attain than was really the case. From the facts then known he was indeed able to deduce a considerable series of general principles, and by their aid could predict the nature of a reaction, provided that the properties of the bodies (*i.e.* their state of aggregation) taking part in and resulting from the reaction were known. But the relatively small beginnings of a chemical statics to which these facts led did not serve to satisfy him; and he, therefore, sought to introduce into chemistry other principles, taken from physics and mechanics. This introduction, although plausible to some extent, was not justified by the facts known at that time, nor indeed have later observations served to justify it. In this way Berthollet, as he himself afterwards acknowledged,[1] withdrew from his own principia and so brought discredit on his correct and well-founded theory.

[1] *E.g. Ann. Chim.* lxxvii. p. 295 (March, 1811), in remarks to a paper by Pfaff, Berthollet says: 'J'avoue que je me suis écarté de mes principes, en regardant la capacité comparative de saturation comme une mesure absolue de l'affinité,' etc. See also 'Troisième suite des recherches sur les lois de l'affinité,' § xvii. p. 288 (*Mém. de l'Inst.* vii. part. i. p. 229, 1806).

Berthollet greatly aided our insight into chemical phenomena by submitting the influence of the mass of the reacting substances to a vigorous examination. In many cases he showed that the relative quantities of the substances and their state of aggregation determine the character of the phenomena by their influence upon the bodies taking part in the reaction. These doctrines of Berthollet have not been lost, though they are now regarded more as useful hints for the practice of chemical analysis than as fundamental scientific laws.

Berthollet believed it possible to show that the influence of mass could be explained mathematically, but attempted this in an unjustifiable manner. He fell into the fallacy of supposing that since the reaction is proportional to the mass taking part in it, then in the production of any compound the larger the amount of any given constituent present, so much the more of the same will enter into this compound. Closely allied to this view is that which regarded the capacity of saturation of acids and bases, the most active chemical substances, as a means of measuring their affinity. Opposed to both of these views were those of the school, which founded a new epoch in the development of chemistry; this epoch commenced about the time at which Berthollet published his 'Chemical Statics.' The teachings of the new school represented chemical atoms as depending on the reciprocal action of constant weights, viz. the combining or atomic weights.

Berthollet's views led to the celebrated discussion with his countryman Proust as to whether the quantitative proportions in which two or more bodies unite chemically are always constant, or vary continually with external conditions. In this discussion, notable for the pertinacity and the great exercise of ingenuity, as also for the politeness and perspicuity with which it was for many years conducted, Berthollet was worsted by his opponent, who was aided by the investigations of a steadily increasing number of excellent workers.

During this discussion, Dalton's speculations led him to a hypothesis which gave a surprisingly clear explanation of the doctrine of the fixity of composition of chemical compounds, a doctrine which was at that time disputed by Berthollet. This was the atomic hypothesis, which has since become the foundation of chemical science. The theory evolved from this hypothesis gave to chemistry quite a new form peculiarly its own. The determination of the combining or atomic weights of the elements and the proportions in which they unite absorbed for some time the powers of the most gifted men. All phenomena which could not be attributed to fixed atomic proportions were set aside as not truly chemical, and were often neglected. Thus chemists forsook the bridge by which Berthollet had sought to unite the sister sciences, physics and chemistry, in order to follow a new path, which has since led to such exceedingly great results, that scarcely any one science can boast of having made such gigantic strides in its development in half a century.

In the rapid development of the science in this newly opened field of investigation it was natural that the methods of investigation nearly allied to the physical method proposed by Berthollet should, at first at any rate, be disregarded. This happened the more readily since the latter was accidentally based upon a view directly opposed to the new atomic theory. The results of Berthollet's observations on the dependency of chemical phenomena upon the external physical circumstances, on the properties of the substances reacting upon one another and also on those of the products of the reaction, were retained by the science. But affinity alone and the manner of its action formed no longer the chief aim of investigation, for now the products of the reactions were regarded as of the greatest importance. Only as far as the conditions influenced the formation of new and important compounds, did they receive any attention. Even then, as is

now often the case, the physical properties of newly discovered substances received just as much attention as appeared necessary to characterise and identify them. Nevertheless, the first authorities in the science dwelt again and again on the necessity of not neglecting the physical methods of investigation.

It cannot be denied that, by the acceptance and development of the atomic theory, chemistry became more and more estranged from the nearly related science of physics. The provinces of the two sciences were more sharply defined, each discipline pursued its own path and the portions common to both remained often untouched, unless, as was frequently the case, they were appropriated by chemistry alone. Almost daily new relations between chemical and physical phenomena were discovered; but even the greatest discoveries made by the application of physical methods to chemical research did not, since the aim of each had become different, serve to reunite the now severed sciences.

It was now most important for chemists to prepare, study, and classify as large a proportion as possible of those compounds the existence of which was predicted by the atomic theory. Thus chemistry assumed more and more the form of a descriptive natural science, in which general theoretical speculations, such as those to which Berthollet had attached first importance, became now of secondary import only. This change was necessary. As geology requires mineralogy and paleontology, as the physiology of plants and animals requires systematic botany and zoology, together with the anatomy of the two kingdoms; or in more general terms, as each speculative science requires a rich and well ordered material, if it is not to lose itself in empty and fruitless fantasies; so also a theoretical chemistry requires the exact knowledge of an extremely large number of chemical compounds, for without such a knowledge chemistry would soon run the danger of being stranded. When the enormous

material, which appears to tower higher and higher as we advance, has been arranged and classified by the untiring zeal of the most gifted investigators, then only can we think of laying the foundation of a building, which perhaps in the next century will develop into a theory of chemistry—a theory such as that of light and of electricity, by means of which from given conditions phenomena may be predicted.

Chemistry is still far distant from the goal which Berthollet desired to reach; but still much has occurred which indicates that the science will continue to strive successfully to gain this point. The chemistry of the present day resembles a plant, which spreading its roots in the ground and collecting food prepares for a later and quick growth of branches, leaves and fruit. The rich material which the rapid development of the atomic theory has furnished insures a lasting independency to chemistry; it will never be again a dependency or subdivision of physics.

But as no branch of human knowledge can be developed in any one direction without at the same time enriching other and neighbouring ones, so a systematic and descriptive chemistry could not be developed without adducing a rich material for the theoretical or speculative portions of the science. Chemists have employed almost all physical methods to decompose known bodies and to prepare new ones. Moreover, as a knowledge of the physical properties of many thousand compounds appeared important for their classification, they have been therefore more or less thoroughly investigated. By this means many new and general points of view have been obtained, which elucidate the dependency of chemical phenomena upon the physical conditions under which they take place, and also the relation of the physical properties of bodies to their chemical composition.

But however great the importance and interest of these discoveries, no theory deduced from them has made itself so

quickly and certainly felt as the atomic theory of Dalton. Almost all these theories have met with severe opposition, many have been overthrown, whilst others have only after some years been deservedly acknowledged. It is indeed a sure sign of the healthy development of our science, that while the knowledge of facts has increased with extraordinary rapidity the generalisations which could have been drawn from them have met with but relatively tardy recognition. With such a subject in which something new was to be expected almost day by day, every generalisation was, after a few steps, in danger of meeting some fact by which it would be either overthrown or considerably modified. Hence the necessity for careful generalisation. If chemistry had acknowledged and accepted every theory proposed, it would have been easily converted into a chaos from which the possibility of generalising would have entirely disappeared.

Having as a rule recognised this danger, the chemists of our century have throughout been very careful even in the formation of general theories, as also in the recognition of those theories which have been accepted at least by some chemists. It might be more justly said that this opposition has been too strong rather than too weak; for many of the theories now accepted with perfect justice had to fight in vain for years with difficulties of but little real importance. They were only accepted when this opposition had strengthened and made them more sure; others again received a tardy but uncontested recognition as the number of facts upon which they were based increased, although at first but little attention was paid to them. Some few theories only have enjoyed for a time a greater renown than they deserved or were able to support.

There was still another circumstance which, throughout the first half of this century, hindered the development of general chemical theories, viz. the condition of physics and its

relation to chemistry. It is natural that a fundamental hypothesis explaining the properties of matter should not remain confined exclusively to the province of chemistry, but must moreover agree with the fundamental ideas and general doctrines of physics, and thus receive a direct confirmation.

At the beginning of this present century, when chemistry guided by the atomic theory began its new and brilliant development, physics was not in a position to follow. Although the speculations of physicists were apparently based upon the existence of the smallest particles of matter, and although such expressions as molecules, pores and interstices, were used by them, yet their calculations were in reality based upon the doctrine of the homogeneity and continuity of matter, and not upon the existence of single atoms, without the acceptance of which chemical teaching could no longer exist.

The only physical theory which was in reality based upon the action of the smallest particles was that of heat. This theory was based upon views which hindered the development of and introduced great confusion into theoretical chemistry, viz. the notion of the material existence of heat.

Although as early as 1798 Benjamin Thomson, better known as Count Rumford,[1] had convincingly shown that heat is nothing more than a form of motion, yet opposed to the recognition of this doctrine was Newton's emission theory of light, a theory which was generally accepted at that time. Even Humphry Davy,[2] although he immediately declared

[1] *Lond. Phil. Trans.* 1798, lxxxviii. p. 80, 'An Inquiry concerning the Source of Heat excited by Friction.' By Benjamin Count Rumford (xviii. p. 278 in the abridged edition of *Phil. Trans.*) In this paper Rumford says: 'It is hardly necessary to add, that any thing which any *insulated body* or system of bodies can combine to furnish *without limitation*, cannot possibly be a *material substance*: and it appears to me to be extremely difficult, if not quite impossible, to form any idea of anything capable of being excited and communicated in these experiments, except it be *motion*.

[2] 'Researches on Heat, Light and Respiration,' in Dr. Beddoe's *West Country*

himself in favour of Rumford's views, and confirmed them by carefully chosen and convincing experiments, nevertheless still upheld Newton's emission theory and opposed the undulatory theory proposed and defended by Hooke, Huygens and Euler.[1] The establishment of this theory is mainly due to Fresnel; Thomas Young and Wollaston had in vain attempted to bring this about; further, Poisson brought it into agreement with mathematical theories, by regarding the ether as composed of discrete particles and not as a continuous elastic medium. The establishment of this theory formed a basis for the mechanical theory of heat, a theory which has since been brilliantly developed, and thus a new point of union between chemical and physical theories has been attained.

One of the most important requirements for the completeness of a general chemical theory is still wanting, viz. a theory of electricity which, from a single point of view, can explain the interdependency of the phenomena of electricity with those of light and heat on the one hand and the chemical forces on the other. But the present condition of the mechanical theory of heat, especially the theories of molecular physics deduced from it in recent times, together with the views which chemists hold regarding the constitution of compounds, show that without the aid of such a theory of electricity, important results may be expected from the mutual employment of physics and chemistry.

The respective positions of each of the sciences are, however, such that they cannot mutually aid one another, even to a small extent, without further development. They are still regarded as entirely distinct from one another. Physics may possibly already possess many of the means which might lead

Contributions, p. 16 (compare also Joule, *Phil. Trans.* 1850, part I. p. 61); further, vide *Elements of Chemical Philosophy*, div. I. chap. v. collect. works, 1840, iv. p. 66.

[1] *Elements of Chemical Philosophy*, div. II. chap. iv. collect. works, iv. p. 157; 'Researches on Heat,' etc. p. 10, etc.

to a comprehensive theory of chemical and physical molecular actions. The methods of mathematics may also be sufficiently advanced to render if required a successful aid to speculation as soon as the phenomena have been analysed and well chosen hypotheses have been found to form the starting point of the theories required. The empirical material, however, which these theories should embrace is almost unattainable to physicists, and can only be arrived at by a thorough and detailed study of modern chemistry.

The process of development of chemistry has been such that each theoretical view could only be deduced from a large and often widely distributed number of facts. Hence arose the feeling of uncertainty or doubt as to the value of theoretical considerations generally, which frequently led to speculations concerning the origin and nature of phenomena being incidentally announced or but hinted at, and even in some cases not expressed but left to the reader to deduce. Further, the most contradictory views have been promulgated, and it has rarely happened that such views have been expressly withdrawn. Which theories are recognised and which discarded, living chemists are alone able to judge, and expressions of such opinions find a place in their writings in exceptional cases or in fragmentary forms only. From the literature alone the difference of views appears greater than it really is; this difference is, however, but a slight one as regards important matters.

The discussion concerning the systematic arrangement of chemistry appears to have lapsed for some time to come. The question discussed for years under various forms and with considerable energy, as to whether the properties of chemical compounds depend more upon the nature than upon the arrangement of the constituent atoms, has been settled, both parties having established their justification. Chemical symbols and formulæ, which a few years ago received such pro-

minence, are now regarded with indifference, since what was formerly expressed symbolically and indistinctly or even without proof or clearness by their aid, can now be expressed in clear words with fixed meaning. The dogma that the atomic constitution of matter is beyond our knowledge has disappeared. It is indeed probable that this idea was in reality never entertained by a single chemist, but was nevertheless frequently used by speculative thinkers, as the most important support of their polemics: it has now no longer any power or authority. Much is already known of the behaviour of atoms in compounds; we shall still learn more, and the present development of chemistry will be one day crowned with a knowledge of the statics and mechanics of atoms. By the aid of such knowledge it will be possible to explain, from a common standpoint, the causes of the innumerable phenomena which we at present can only classify.

The feeble beginnings of such a theory are not only dispersed through the whole province of the science, but are clothed in the most varied and heterogeneous forms. Chemistry will, in fact, still continue to use the symbols of opposing views, even where the differences of meaning have ceased to exist. The strife between the opposing views has been fought out within the chemical camp alone, yet sufficient intimation has reached other scientific men to awaken amongst them a lively interest in the result. The interest is probably heightened by the difficulties, which one not versed in chemistry must surmount in order to obtain a valuable insight into the subject. Chemists, therefore, often hear the representatives of the most varied natural sciences express the desire of obtaining a nearer insight into the modern chemical theories, and the wish is often accompanied by the desire that such a review should not necessitate too much special study.

This wish so often expressed has chiefly influenced me in undertaking the experiment of bringing together the apparently

best founded portions of the hypotheses and theories at present of value in chemistry, and to represent them stripped as far as possible of their purely chemical character and so render them available to a wider circle of readers.

Chemists perhaps will also welcome the publication of the views and opinions which in the course of time have received some recognition. These theories will be more interesting when treated as an organic whole than when scattered and isolated.

In the following pages I have endeavoured to arrange *sine ira et studio* the older and the more recent theoretical chemical results which appear to have attained a certain degree of polish and of accuracy, and may therefore be regarded as affording a special insight into the conditions of equilibrium of the smallest elementary particles. It is to be hoped that this representation will be found to be as free as possible from preconceived ideas, which have often warped and may still warp the judgment, as to the admissibility of a conclusion.

Chemists will find but little that is new, and even the method of statement is at the most a little more defined than was formerly customary or thought advisable. The merit of rendering a service to science by means of this book is equally shared by the author and the colleagues with whom this subject has been frequently discussed.

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MODERN THEORIES OF CHEMISTRY.

THE ATOMS.

I.

THE ATOMIC HYPOTHESIS THE BASIS OF ALL VALID CHEMICAL THEORIES.

§ 1. This hypothesis assumes that all varieties of matter are composed of aggregations of a large number of exceedingly minute isolated particles called atoms; even those forms of matter which appear to completely fill the space they occupy being no exception to this rule. It also assumes that there are as many different kinds of atoms as there are different kinds of undecomposable substances. This hypothesis, which is closely related to the views held by the ancient Greek philosophers, owes its present form in the first place to chemical discoveries, but is thoroughly in agreement with the results of physical investigation; so much so that in the present state of speculative natural science no theory is acceptable which is not founded on the hypothesis that matter is composed of separate and distinct particles. The truth of this theory is not at first sight apparent, being, in fact, discordant to the feelings of the uninitiated, and introduces also in many cases inconveniences in the development of theories in mathematical physics, by its increase in the difficulties of the calculations; nevertheless it is indispensable, since observed phenomena can only be accounted for on the assumption of the existence of distinct particles of matter. This conclusion must be universally accepted by physicists and

chemists. Many of the reasons which led to its acceptance have been exhaustively discussed by Fechner.[1]

It would not be difficult to strengthen the grounds for its adoption by entering into a further consideration of special cases. Here, however, it will be sufficient to point out that without an atomic theory in chemistry every possibility of a theory, even of a concrete representation, would cease to exist. Nevertheless, attempts have frequently been made to replace the atomic hypothesis, but none of these attempts have proved of any service to the science. Up to the present day no hypothesis has been brought forward the deductions from which agree so closely with observed facts as do those based on the atomic hypothesis.

We start, then, with the idea that matter consists of particles called atoms, of which we assume that there are as many varieties as there are different kinds of simple bodies, or what are called chemical elements. Whether these traditional particles called atoms are really *ἄτομοι*, *i.e.* bodies absolutely indivisible, is not even probable, and is a matter of little moment. But it is sufficient for our purpose to state that at the present time we are not able to split them up. Whether in the future the question of their divisibility will be solved can have no influence in the discussion of the present subject.

§ 2. The chemical atomic theory owes its foundation and its acceptance to the observation that the union of different chemical elements to form a new compound always takes place in definite proportions, according to the so-called combining or equivalent weights.

If M, M_1, M_2, &c., represent the fixed and definite combining weights of different elements, the composition of any chemical compound can be expressed by the formula—

$$nM + n_1M_1 + n_2M_2 + \ldots .$$

where the coefficients n, n_1, and n_2 signify whole numbers, which may have different values in different cases.

For instance, mercury combines with oxygen in two different proportions. Mercuric oxide contains 12·51 parts by

[1] *Ueber die physikalische und philosophische Atomenlehre*, von G. T. Fechner. Leipzig, 1855. 2. Aufl. 1864.

weight of mercury to 1 part of oxygen, whilst mercurous oxide contains double the quantity of mercury, viz. 25·02 parts.

Mercuric oxide is therefore represented by $1\ M + 1\ M_1$, and mercurous oxide by $1\ M + 2\ M_1$, when the ratio between the combining weights of oxygen, M, and mercury, M_1, is as 1 : 12·51.

The absolute numerical values attached to the combining weights depend on the unit of weight chosen. If the combining weight of oxygen is selected as unit, then $M = 1$ and $M_1 = 12{\cdot}51$.

In cinnabar this quantity of mercury is combined with 2·004 parts by weight of sulphur, the lower sulphide only containing half as much sulphur, or twice as much mercury to the same amount of sulphur.

The sulphides of mercury are therefore represented by—

$1\ M_1 + 1\ M_2$, Mercuric sulphide;
$2\ M_1 + 1\ M_2$, Mercurous sulphide;

when $M = 1$, and $M_2 = 2{\cdot}004$.

The combining weight of sulphur deduced from these experiments is available for other compounds of sulphur, *e.g.* for its compounds with oxygen.

Sulphurous anhydride, $2\ M + 1\ M_2$;
Sulphuric anhydride, $3\ M + 1\ M_2$;

where $M = 1$, and $M_2 = 2{\cdot}004$.

We are also acquainted with compounds containing mercury, sulphur, and oxygen; the composition of certain of these bodies may be represented thus:—

Mercurous sulphate, $4\ M + 2\ M_1 + 1\ M_2$;
Mercuric sulphate, $4\ M + 1\ M_1 + 1\ M_2$;
Turpeth mineral, $6\ M + 3\ M_1 + 1\ M_2$; &c.

The proportional weight with which a given element unites with any other is the same for all the compounds it forms with the other elements. It is a constant, depending solely on the nature of the particular element.

Dalton's atomic theory[1] explains these facts by the as-

[1] For the rise and development of this doctrine see H. Kopp's *Geschichte der Chemie*, ii. 385.

sumption of chemical atoms which unite together in groups, forming by their union the smallest particles of those bodies we call chemical compounds. The groups of atoms so formed differ from each other in the number and nature of their constituent atoms. M, M_1, M_2, &c. represent the weights of these atoms; and the coefficients n, n_1, n_2 express the number of atoms entering into combination. Each individual compound is characterised by the composition and internal arrangement of the groups of atoms or molecules of which it is composed.

The introduction of the atomic hypothesis immediately after the enunciation of the principles of the science by Berthollet, effected a complete change in chemical statics and dynamics; and has contributed largely to the development of this branch of the science.

§ 3. A knowledge of the atoms and molecules is an imperative necessity, since it is of their equilibrium and motion that the doctrine treats. The determination of the atomic weights has therefore become one of the first problems of theoretical chemistry. Attempts to determine the weights of the atoms were for many years unsuccessful, and even at the present time they cannot be ascertained with a sufficient degree of accuracy; we have, therefore, been compelled to content ourselves with a knowledge of their relative value. The weights of all the different kinds of elements are expressed in terms of any one given atom. In recent times the weight of an atom of hydrogen, which was originally chosen by Dalton as the standard of comparison, is taken as the unit, as it is the lowest value; but formerly the example of Wollaston and Berzelius was followed, who referred the atomic weights to that of oxygen, which was taken as 1, 10, or 100.

Berzelius introduced into the science the use of the initial letters of the names of the different elements as convenient symbols for representing the weights of the atoms expressed in terms of the conventional unit.[1]

But even the relative weight of the atom cannot be directly determined. The determination is based in the first place on an empirical investigation of the combining or proportional

[1] *Lärbok i Kemien*, af Dr. J. J. Berzelius. Tredje delen. Stockholm, 1818, p. 94.

weights according to which the elements combine. But since our analyses and syntheses only show the relative quantities of the constituents of a compound, but not the number of atoms (the values n_1, n_2, n_3, &c. in the previous formula) which are combined together at first, it remains doubtful whether the combining weight found by experiment corresponds with and is proportional to one or more atoms.

The quantities Q, Q_1, and Q_2 (found empirically by analysis) of the constituents of a compound admit of different significations. They must stand in a definite relation to each other and to the atomic weights of the elements. For example, if a compound contains the quantity Q of one element and Q_1 of another, then the following proportion must exist: $Q : Q_1 = nA : n_1 A_1$, when A and A_1 are the atomic weights of the two elements, and n and n_1 represent whole numbers.

But since not only the atomic weights A and A_1, but also the coefficients n and n_1, are unknown, it is obvious that the atomic weights cannot be determined from the knowledge of the equivalent proportions alone.

It is on this account that the atomic weights of many, if not of all the elements, have had several values attributed to them at various times and by different investigators. The accurate determination of the relative atomic weights has, indeed, frequently been declared to be a problem incapable of solution, and consequently attempts have been made to replace the more or less hypothetical atomic weights by the so-called equivalent weights, which were supposed to be purely empirical. But this attempt encountered many difficulties, and in recent times atomic weights are once more employed in the original sense.

§ 4. There is essentially a close relation existing between the properties of an element and its atomic weight; and since the promulgation of the atomic theory many attempts have been made to arrive at the atomic weights by means of this relationship, but it is only in quite recent times that it has been possible to do this with any degree of accuracy. The most important expedients for ascertaining these are, in the first place, the determination of the density in the gaseous state, and in addition to this, the determination of the capacity

for heat in the solid state of an elementary body. The connection between these two values and the chemical units was pointed out at the beginning of the present century by Gay-Lussac (1808) and by Dulong and Petit (1819), but their range and applicability were for many years undervalued and unappreciated, because the results obtained by the two methods could not be brought into unison. Until the year 1858 it was generally believed that, for one series of elements, the density in the gaseous state corresponded to an atomic weight different from that indicated by the specific heat. Cannizaro [1] then pointed out that this apparent contradiction arose entirely from an incorrect interpretation of well-known facts, the true signification of which had been correctly indicated by Avogadro.

Each of these important experimental methods now began to meet with the appreciation to which it was justly entitled. Isomorphism, discovered by Mitscherlich in 1819, offers a third valuable method, which is, however, not so trustworthy as the two others, but is often employed when the others cannot be used.

On the other hand, Faraday's important law of electrolysis, formerly believed by many chemists to be an auxiliary in the determinations of atomic weights, has proved of little service, electrolytic equivalents not being identical with the atomic weights.

[1] *Sunto di un corso di filosofia chimica.* Pisa, 1858. See also Kopp and Will, *Jahresbericht*, 1858, 11.

II.

THE DETERMINATION OF THE ATOMIC WEIGHT FROM THE DENSITY IN THE GASEOUS STATE.

§ 5. Gay-Lussac [1] discovered that the densities of different gases, whether simple or compound, when measured under the same pressure and temperature, are either proportional to or are simple multiples of their empirical combining weights.

If two gases take part in a chemical reaction, the volumes of the combining or mutually decomposing gases (under similar conditions of temperature and pressure) [2] are either equal, or they bear a simple relation to each other; and similarly the volume of the product of combination or decomposition, if it is capable of existing in the gaseous state, always exhibits a simple relation to the volume occupied by its constituents in a similar state before the act of decomposition or combination.

According to Dalton's atomic theory, and the facts on which it is based, every act of chemical combination or decomposition is a mutual action between a definite number (usually small) of atoms.

Hence it follows, from Gay-Lussac's discovery, that the number of atoms which are contained in a given volume of any substance in the gaseous state stands in a simple ratio to the number of atoms contained in the same volume of any other gas under the same pressure and at the same temperature. The absolute numerical value of this ratio is at first undecided. It follows from the atomic doctrine and from Gay-Lussac's law that if one gas contains x atoms in a given volume, a second will contain $\frac{n}{m}x$ atoms in the same

[1] *Mém. d'Arcueil*, ii.

[2] Equality of temperature and pressure is always assumed, even when it is not expressly mentioned.

space, where n and m represent small whole numbers. The absolute value of these numbers can only be determined by introducing new hypotheses into the theory.

§ 6. The simplest, and apparently the only trustworthy hypothesis conceivable on this point is the explanation proposed by Amadeo Avogadro [1] in 1811, which is at the present time accepted by the majority of chemists.

Avogadro assumed that the number of particles into which a substance splits up in its conversion into the gaseous state is the same for equal volumes of all gases without exception, under similar conditions of temperature and pressure, and therefore that the weights of the particles are proportional to the densities of the gases observed under similar external conditions. Avogadro called these smallest particles *molécules intégrantes* or *constituantes*, and defined them as particles of matter which are so far apart that they no longer exert any mutual attraction, but are merely subject to the repelling action of heat.

Avogadro stated that the similarity in the behaviour of all gaseous substances under the influence of temperature, pressure, &c., could only be explained on the assumption that equal volumes of different gases contained the same number of such particles or molecules.[2]

The fact that Avogadro intended to apply this hypothesis to all gases without exception was for many years neglected. Until recently it was customary to apply it unscientifically, making a distinction in its application, to the class of so-called elements on the one hand, and to the class of compound bodies on the other; but Avogadro's assumption that there is no difference in this respect between simple and compound bodies was lost sight of, although Avogadro had in the most simple and felicitous manner overcome the only apparent obstacle to this view.

[1] *Essai d'une manière de déterminer les masses relatives des molécules élémentaires des corps, et les proportions selon lesquelles elles entrent dans les combinaisons*; par A. Avogadro. *Journ. de phys. &c.*, par Delamétherie, 73, Juillet 1811, 58–76. 2nd part; *ibid.* Fév. 1814.

[2] Since Avogadro believed in the material nature of heat, he states in his hypothesis that the distance between the molecules, or, what is the same thing, the diameter of their heat atmospheres, is the same for all gases under similar external conditions.

§ 7. This difficulty arose from a tendency to consider these gaseous particles, viz. the molecules of the elementary gases, as identical with their chemical atoms, for which there is no sufficient reason. Avogadro avoided the difficulty by simply denying their identity, and by assuming, on the contrary, that even the molecule of the simple gases is a mass which is divisible by chemical action, the limit of divisibility of which can only be experimentally determined.

He regarded the molecules as groups of several individual atoms (*molécules élémentaires*) united by mutual attraction to form a compound. There is nothing inconsistent in this hypothesis, since the assumption of mutual attraction, cohesion, or molecular attraction, even between particles of the same nature, cannot be avoided in chemistry any more than in physics, in spite of the different views which may be held concerning the nature and cause of the attraction. Avogadro made an exhaustive application of his views to all the then known examples of the combination and decomposition of substances in the gaseous state. He pointed out that in each single gaseous compound known the volume it occupies is double that of the element uniting with one or more volumes of the other element.[1]

It is also possible for the compound to occupy four times the volume of one of its constituents. In the first case he concludes that the molecule of this constituent must have split up into two parts; each molecule of the compound would then contain only half a molecule of this element. In the second case the molecule would have divided into four parts.

§ 8. On pages 70 and 71 of his treatise Avogadro speaks of the formation of hydrochloric acid from chlorine[2] and hydrogen. One volume of chlorine unites with one volume of hydrogen to form two volumes of hydrochloric acid.

If equal volumes of each of these three gases contain the same number of particles or molecules, then after the act of combination there must be twice as many molecules of hydro-

[1] Some cases of combination without the volume being doubled have since been discovered.

[2] Like Davy, he regarded chlorine as an element, contrary to the opinion of most of his contemporaries.

chloric acid as there were previously molecules of hydrogen and chlorine, therefore each molecule of the compound can only contain half a molecule of each constituent.

Similarly he points out, in a note to page 60, that the molecule of water is formed of half a molecule of oxygen and a whole or two half-molecules of hydrogen; and in like manner he discusses the composition of all the gases which were known at that time. Avogadro does not expressly state what relations the particles which he calls molecules bear to the atomic weights; but his remarks undoubtedly show that he did not regard them as identical, but that, on the contrary, he clearly recognised the fact that the combining weights or atoms are as a rule only fractions of molecules. This difference was for many years entirely overlooked. Even Berzelius [1] declared that Dumas' defence of Avogadro's views was absurd, as he assumed a division of the indivisible atoms.

§ 9. In 1814 Ampère published an article [2] in which he promulgated similar opinions to those advocated by Avogadro. He attempted to gain a definite conception concerning the number and arrangement of the elementary atoms [3] which form the molecules [4] of different substances. It is worthy of remark that, a short time before, H. Davy [5] had declared himself in favour of the view that the atoms first combine to form regularly arranged groups, and that bodies are composed of these groups, acting as elementary particles.

§ 10. Although these speculations attracted the attention of chemists, they did not gain the complete recognition and general acknowledgment which their supporters desired. These

[1] *Jahresb.* 1826, 80.

[2] 'Lettre de M. Ampère à M. le comte Berthollet sur la détermination des proportions dans lesquelles les corps se combinent d'après le nombre et la disposition respective des molécules dont leurs particules intégrantes sont composées,' *Annal. de Chim.* xc. 43. Ampère's views are less simple than Avogadro's, since his particles are intended to be identical with the elementary particles which determine the crystalline form of bodies. To these Haüy has given the name of 'molécules intégrantes.' Avogadro regarded this extension of the hypothesis as unjustifiable. See the latter's *Fisica de' corpi ponderabili*, 1838, ii. 854.

[3] 'Molécules.' [4] Called 'particules' by Ampère.

[5] *Elements of Chemical Philosophy*, Div. I. vi. p. 124, in the edition published in 1812. Collected works, 1840, iv. 90.

hypotheses and theories had to pass through an experience similar to that of many others. 'The first attempt at generalisation seldom succeeds; speculation anticipates experience, the results of observation accumulating but slowly.' [1]

In the existing state of the science there was no pressing necessity to accept Avogadro's hypothesis and the theories derived from it, and the material at hand was not then sufficient to permit of a moderately wide application of his views. Avogadro, therefore, endeavoured to apply the results gained from the consideration of gaseous bodies to cases where no observations whatever of the density in the gaseous state had been made. In this way a source of great uncertainty was brought into the new theory, which lowered its value in the eyes of chemists perhaps more than the absence of the attempted extension would have done.

Half a century after the promulgation of Avogadro's hypothesis, the rapid development of organic chemistry, and more especially the knowledge of the density of the gases or vapours of those bodies which only assume the gaseous state at high temperatures, first called attention to the necessity for a logical and universal application of this hypothesis, and of the theories based on it. The honour of successfully striving to attain this desired end is especially due to Dumas, Gerhardt, and Laurent. But the reasons by which these and most other investigators were influenced in favour of Avogadro's hypothesis were essentially different from Avogadro's. They were entirely derived from the behaviour of different substances in acts of chemical decomposition and combination. A few isolated arguments in support of Avogadro's views were, indeed, derived from the physical properties of bodies—*e.g.* by H. Schröder [2] from the boiling-points of organic compounds. But these arguments produced no permanent effect, whatever their intrinsic value may have been.

Avogadro's hypothesis was adopted because the molecular weights determined by its aid appeared the only numbers capable of serving as the basis of a theoretical speculation on

[1] Berzelius, *Jahresb.* 1830, 213.

[2] *Die Siedhitze der chemischen Verbindungen*, 1844, pp. 27, 67, 138; *Pogg. Ann.* 1845, lxiv. 399.

all the different chemical transformations, and especially because this hypothesis established an analogy between the so-called elements and their compounds, by regarding the former as compounds of similar atoms, and the latter as compounds of dissimilar atoms. This analogy was afterwards observed in many other cases. An important indication of the necessity for the adoption of this hypothesis is the fact that at the very time when chemists were actively discussing this question, Clausius,[1] who was not aware of the discussion,[2] independently recognised the necessity of the hypothesis on purely physical grounds arising out of the mechanical theory of heat.

§ 11. The fact that the general adoption of the molecular weights, determined by Avogadro's law, was only brought about after a complete examination of numerous chemical transformations has led to the erroneous conclusion that the weight and composition of the molecule of any substance can be determined by means of chemical reactions alone, without the knowledge of the vapour density of the substance.

A molecule has accordingly been defined as the smallest quantity of a substance which can take part in a chemical reaction. This and similar definitions are either inexact or incorrect. If by 'smallest quantity' is meant the smallest amount which can take part in any chemical change, then the definition frequently gives a much smaller molecular weight than is accepted by all chemists in accordance with Avogadro's law. For example, without the aid of this law, the syntheses of hydrochloric acid, potassium chloride, silver chloride, &c., from their elements would indicate that that 'smallest quantity' of chlorine is an atom, whereas it is universally acknowledged that two atoms form a molecule. If we represent the first synthesis by the equation—

$$H_2 + Cl_2 = HCl + HCl,$$

it will then be in accordance with Avogadro's conclusion mentioned in § 8; but without this restriction the above definition would lead to the equation—

$$H + Cl = HCl.$$

[1] *Pogg. Ann.* 1857, c. 369. [2] *Ibid.* 1858, ciii. 645.

If, on the other hand, the definition means the smallest quantity which frequently or generally takes part in a chemical reaction, then the definition is variable and arbitrary, and very often leads to other results than the generally accepted deductions from Avogadro's hypothesis. To take a single example: Nitric acid more frequently enters into a chemical reaction in double or treble the amount which is at present regarded as the molecule, and represented by the formula HNO_3, than as a single molecule. If the simultaneous formation of chloride and hypochlorite (that is, of two different chlorine compounds from chlorine and an alkali) is advanced as a proof that each particle of chlorine must contain at least two atoms, then the simultaneous formation of nitrate and nitric or nitrous oxide, &c., from a metal and nitric acid can be used as an argument proving nitric acid to contain more than one atom of nitrogen in the molecule. Nothing is proved in either of these cases, since the amount taking part in the reaction may just as well be regarded as composed of one as of many particles.

That some celebrated chemists believed themselves justified in holding other views was due to the fact that they had a vivid recollection of the arguments which had led them to recognise Avogadro's hypothesis, and consequently they confused the reasons for the adoption of the molecular weights, determined according to this hypothesis, with the speculations which led to the method adopted for their determination.

That the study of chemical reactions for the determination of the molecular weights without the aid of Avogadro's hypothesis is very deceptive and thoroughly inadequate is seen from the fact that molecular weights which were quite different from Avogadro's were for many years used in representing chemical reactions, and were universally regarded as satisfactory.

But the examination of chemical transformations affords invaluable assistance in confirming the accuracy of the molecular weights calculated from the vapour densities by means of Avogadro's law, since it shows that chemical reactions can, as a rule, be represented in a very simple manner by means of these molecular weights.

§ 12. The space at our disposal neither permits of an approximately exhaustive statement of all the reasons, deduced from numerous chemical facts, which testify to the correctness of Avogadro's hypothesis, nor of the marked influence which its introduction has exerted on chemical theories. But this can all the more reasonably be dispensed with, since a complete discussion of this hypothesis is to be found in almost all the modern treatises on chemistry.[1]

Every reader, therefore, can easily form a judgment of the advantages which this hypothesis affords for the explanation of chemical changes. The arguments derived from the observation of chemical phenomena do not in general appear of great importance when taken separately. No particular one of them decided the acceptance of the hypothesis. They gradually gained force in consequence of their large number and mutual agreement, therefore the hypothesis of Avogadro on molecular values only received a gradual recognition. It grew in favour as the number of facts increased which could be simply and naturally explained by its aid. Owing to this mode of deve-

[1] The following works may be consulted on this subject:—

C. Gerhardt, *Traité de Chimie organique*, iv. (Paris, 1856.) Gerhardt's system, founded on Avogadro's hypothesis, possesses historic interest, inasmuch as it forms the basis of the generally accepted systematic course of organic chemistry.

Aug. Laurent, *Méthode de Chimie*. (Paris, 1854.)

Aug. Kekulé, *Lehrb. der organischen Chemie* (Erlangen, 1859–67), which exerted a great influence on the recent development of theoretical chemistry.

Herm. Kopp, *Lehrb. der physikalischen und theoretischen Chemie*, 2. Aufl. (Braunschweig, 1863); also Kopp's introduction and conclusion to the 14th and 15th editions of Wöhler's *Grundriss der anorganischen Chemie* (Leipzig, 1868 and 1873). The former work contains the most complete description which has yet been published of the theories and facts which the development of theoretical chemistry has produced. The latter work is a concise abstract of the most essential points.

Ad. Wurtz, *Leçons sur quelques points de philosophie chimique*. (Paris 1864.) This book, which appeared almost simultaneously with the first edition of *Die modernen Theorien*, covers the same ground as this work, but treats the subject chiefly from a chemical point of view. It has been revised and published under the title *La théorie atomique* (Paris, 1879), the *Modernen Theorien* having evidently been frequently consulted for this purpose.

A. W. Hofmann, *Einleitung in die moderne Chemie*. (Braunschweig.) A description of the most important results of Avogadro's hypothesis, illustrated by carefully selected experiments and demonstrations.

lopment, chemists long regarded Avogadro's hypothesis as purely arbitrary, and considered it a matter of no importance whether the hypothesis was accepted or disregarded. But, leaving these arguments out of consideration, it is very difficult, if not impossible, to explain known facts from a common standpoint on a physical basis unless it is by the aid of Avogadro's hypothesis. The difficulty will always remain, whatever views are held concerning the nature of the gaseous state of aggregation.

§ 13. Avogadro, like most of his contemporaries, still adhered to the doctrine of the material nature of heat, and consequently explained the expansion of gases by the repulsion exerted between the layers of heat surrounding the individual molecules. He had already pointed out this difficulty (p. 58, *loc. cit.*): 'En effet si l'on supposait que le nombre des molécules dans un volume donné fût différent pour différens gaz, il ne serait guère possible de concevoir que la loi qui présideroit à la distance des molécules pût donner, en tous cas, des rapports aussi simples que les faits que nous venons de citer nous obligent à admettre entre le volume et le nombre des molécules.'

In fact, starting from the assumption that a gas forms a system of particles of matter, whose mutual repulsion produces an expansive force, then the relation which has been found to exist between volume, pressure, and temperature, viz. Boyle's or Marriotte's law and Gay-Lussac's law on the alteration of pressure or volume with the temperature, is only conceivable if Avogadro's view be accepted that all gases contain an equal number of molecules in the same volume, under similar conditions of temperature and pressure. The only other possible hypothesis is that one group of gases contains the same number of molecules, a second group exactly double, and a third exactly three times as many molecules as the same volume of hydrogen or any other gas under the same pressure and temperature.

But this hypothesis offers no means of explaining why the expansive force, and its changes with the temperature and with the change of volume, should be the same for all gases, merely under these conditions. But a detailed examination

of these relations is unnecessary, since the opinion that the expansive power of gases is produced by an actual repulsive force between the molecules is untenable. The deductions from the mechanical theory[1] of heat have shown, and the experiments which were made to test this theory and to determine the constants occurring in it have proved, that scarcely any perceptible amount of internal work is done during the alteration in the volume of gases; the nearer the gas approaches the condition of the ideal permanent gas, the smaller the amount of work required.

But this small amount of work which observation has shown to be required is such as is requisite in surmounting an obstacle to expansion, *i.e.* a slight mutual attraction, not a repulsion, of the molecules.[2]

The spontaneous expansion of a gas does not arise from the mutual repulsion of its molecules. On the contrary, the facts at present known concerning the nature of the gaseous state of aggregation appear only to admit of the view on which Clausius,[3] Maxwell,[4] and other investigators have founded their comprehensive theory. It starts from the old theory,[5] which had been almost forgotten since the beginning of this century, that the conversion to and the existence in the gaseous state are due to an increase in the internal motion of the bodies which is imparted to them in the form of heat,

[1] Clausius, *Pogg. Ann.* lxxix. 392. *Gesamm. Abhandl.* i. 42; 2. Aufl. 46.

[2] W. Thomson and J. P. Joule, *Lond. Phil. Trans.* 1853, cxliii. 357; 1854, cxliv. 321.

[3] 'Ueber die Art der Bewegung welche wir Wärme nennen,' *Pogg. Ann.* 1857, c. 353. See also Clausius, *Ueber d. Wesen der Wärme* (Zürich, 1857); also numerous articles in *Pogg. Ann.*

[4] *Phil. Mag.* [4], xix. 20, and 35.

[5] For the history of this hypothesis see Gehler's *Phys. Wörterbuch*, iv. Abtheil 2, 1049; P. du Bois-Reymond, *Pogg. Ann.* 1859, cvii. 490; Clausius, *ibid.* 1862, cxv. 2; Th. Graham, *ibid.* 1863, cxx. 416; O. E. Meyer, *Kinetische Theorie der Gase* (Breslau, 1877), 9. Humphry Davy, in his *Elements of Chemical Philosophy* (towards the end of chap. v., Part I. of his *Collected Works*, 1840, vol. iv. p. 67, 'It seems impossible to account,' &c.), expressed views on the forms of heat motion which bear a striking resemblance to those of Clausius. He distinguished between oscillating, rotating, and rectilinear motion. His ingenious views are distinguished from those of Clausius solely by his being a believer in Newton's Emanation theory, which ascribed the rectilinear motion to the ethereal particles, and not to the gases.

and which produces such a degree of activity that the individual molecules move away beyond the sphere of action of their neighbours, and are no longer retarded by the attraction of the latter, and consequently travel through space along rectilinear paths with the velocity they have once acquired until they come into collision with an obstruction, which they either adhere to or rebound from.

§ 14. The theory founded on this hypothesis is known as the theory of molecular impacts, or the kinetic theory of gases. Its wide and successful development is specially due to the circumstance that the molecules whilst in motion, having severed their connection with others, can scarcely be influenced by molecular forces, which act only at a slight distance, and consequently only obey the general laws of mechanics. Since these laws are better understood than those governing the action of the molecular forces, which can be investigated only with considerable difficulty, it has, therefore, been possible to develop completely this conception of the rectilinear motion of molecules, and to pursue it by the aid of mathematics to its ultimate conclusions.

All the results which the theory has derived from this idea have been found to agree so closely with facts that almost all the properties exhibited by bodies in the gaseous state appear as necessary results of this primary hypothesis. In this way the hypothesis has again gained a high degree of probability, which approaches certainty at least as nearly as the undulatory theory of light.

The theoretical explanation of the pressure of gases has been an important factor in founding and supporting Avogadro's theory. Daniel Bernoulli explained the pressure of a gas as resulting from the numerous violent shocks of its rapidly moving particles on the body subject to the pressure, and he deduced from this view the law discovered empirically by Boyle, but also known as Marriotte's law, that the pressure of a gas is inversely proportional to its volume, and directly proportional to its density. The same considerations also showed that this law is not absolutely true, and that its validity decreases the less completely the particles of gas are withdrawn from the action of molecular forces. The accuracy

of the law diminishes as the volume really occupied by the molecules increases as compared with the actual volume of the gas. This theoretical conclusion has been thoroughly confirmed by the most exact experimental investigations, especially by those of Regnault.[1]

Neglecting this comparatively minute deviation from Boyle's law, the kinetic theory of gases shows that the pressure of a gas is proportional to the mass of the particles contained in the unit of volume and to the square of their velocity, since not only the force, but also the frequency, of the impacts increases with the pressure. Since half the product of the mass into the square of the velocity is known as the kinetic energy, the result of the theory may be expressed thus: the pressure which a gas exerts or is subject to is proportional to the sum of the kinetic energy of the molecular motion of the mass of gas contained in the unit of volume. Equality of pressure arises from the equality of the kinetic energy of the motion of the particles. The pressure alters proportionally with the kinetic energy, independently of the fact whether the change in the kinetic energy of the unit of volume is produced by increase in temperature or by compression of the mass. The kinetic energy of equal volumes of two different gases under the same pressure is equal. But it has been found by experiment that the pressure of every gas is proportional to its density and to its absolute temperature (calculated from $-273°$ C.): hence it follows that for constant density, and consequently for constant volume, the pressure, and therefore the kinetic energy, of the rectilinear motion of the particles varies proportionally with the temperature. Equal increments of temperature impart to equal volumes of different gases measured at the same temperature an equal increase in the kinetic energy of rectilinear motion, whilst that portion of the energy which is imparted in other forms of motion (rotation, vibration, &c.) may vary considerably with the nature of the gas.

Let $\mathfrak{M}$ denote the molecular weight, or more correctly the mass of the molecule, and u its velocity; then the kinetic energy of the mass contained in a given volume of the gas will be represented by the expression $\Sigma \frac{1}{2} \mathfrak{M} u^2$, in which

[1] *Relation des Expériences*, &c. 1er Mém. i. 1847.

the symbol Σ shows that the value $\frac{1}{2}\,\mathfrak{M}u^2$ is true of each particle, and all such values must be added together. If the gas is homogeneous, then all the $\mathfrak{M}$'s are equal, and all the particles have also the same velocity; therefore the sum may be represented as a product, thus: $\Sigma\,\frac{1}{2}\,\mathfrak{M}u^2 = n\,.\,\frac{1}{2}\,\mathfrak{M}u^2$, where n represents the number of molecules contained in the given volume, *e.g.* the unit of volume.

Practically it never happens that all the u's are equal, as can easily be proved theoretically or experimentally. On the contrary, the particles always exhibit greater or smaller differences in their velocities. But a certain velocity, u, can always be taken, which satisfies the equation $\Sigma\,\frac{1}{2}\,\mathfrak{M}u^2 = n\,.\,\frac{1}{2}\,\mathfrak{M}u^2$. It is chosen so that if all the particles had a uniform velocity, the kinetic energy of the total mass would have the value which it in reality possesses. u is the velocity corresponding to the mean value $\frac{1}{n}\,\Sigma\,\frac{1}{2}\,\mathfrak{M}u^2$ of the kinetic energy of a particle.

It also follows from this theory that the relation $p = \frac{1}{3}\,n\,.\,\mathfrak{M}u^2$ exists between Clausius's[1] mean value of the velocity and the pressure p of the gas. In this equation the number n of the molecules contained in the unit of volume of the gas and the mass $\mathfrak{M}$ of the molecule are unknown. But the product of both these unknown quantities is the mass of gas contained in the unit volume, a value which can easily be determined. If we substitute the numerical values of p and of this product in absolute measure, the value in metres for the velocity per second is finally obtained:

$$u = 485^{m}.\sqrt{\frac{1+a\,.\,t}{d}} = 485^{m}.\sqrt{\frac{T}{d\,.\,273}};$$

where d equals the density of the gas in question compared with air at the same temperature and under the same pressure; $a = 0{\cdot}003665$, the coefficient of expansion of the gas; t the temperature calculated from the freezing-point, and T the absolute temperature in degrees centigrade.

[1] *Pogg. Ann.* c. 375: Abhandlungen über Wärmetheorie. 2. Abtheil. 251.

For the freezing-point, that is when $t = 0°$ and $T = 273°$, Clausius has calculated the following values:—

For oxygen $\mathfrak{u}_0 = 461^m$.
For nitrogen $\mathfrak{u}_0 = 492^m$.
For hydrogen $\mathfrak{u}_0 = 1844^m$.

§ 15. If we apply the above equation for the pressure p to different gases existing under the same pressure we obtain the relation—

$$p = \tfrac{1}{3} n_1 \cdot \mathfrak{M}_1 \cdot \mathfrak{u}_1^2 = \tfrac{1}{3} n_2 \cdot \mathfrak{M}_2 \cdot \mathfrak{u}_2^2 = \&c.$$

where the different values of the various gases are distinguished by different indices. This expression means that the total kinetic energy of the motion of the molecules of different gases contained in equal volumes is equal under the same pressure.

Admitting Avogadro's assumption that under similar conditions of temperature and pressure $n_1 = n_2 = n_3 = \&c.$ that is, that the numbers of molecules in equal volumes is the same for all gases, then it follows that—

$$\tfrac{1}{2} m_1 \mathfrak{u}_1^2 = \tfrac{1}{2} m_2 \mathfrak{u}_2^2 = \tfrac{1}{2} m_3 \mathfrak{u}_3^2 = \&c.$$

The mean value of the kinetic energy of the individual particles is the same in all gases at the same temperature. The reverse of this proposition can be used as a definition of temperature, thus:—The temperature of two gases is equal if the mean value of the energy of the rectilinear motion of their molecules is equal; the mean values of the velocities are inversely as the square roots of the molecular weights.

If Avogadro's hypothesis is not accepted, and if the existence of an equal number of molecules in equal volumes is not assumed—*e.g.* only half as many molecules of hydrogen as of oxygen—then very strange conclusions are suggested. Oxygen and hydrogen would then possess the same temperature if the kinetic energy of the molecules of the latter were exactly double that of the oxygen molecules. It would at least be very difficult to comprehend why this relation should remain in a mixture of the gases where a frequent impact of their

molecules must of necessity take place. Whilst, on the other hand, the assumption is very plausible that equilibrium of temperature consists in equality of kinetic energy, and that the equilibrium results, if not already existing, from the fact that the molecules possessing greater kinetic energy continue by their frequent impacts to impart some of it to those possessing less, until it becomes equalised.

This hypothesis, and consequently the hypothesis of an equal number of molecules in equal volumes, appears to be the only possible assumption if certain general considerations are taken into account, which were first drawn attention to by J. C. Maxwell,[1] and were afterwards extended, and also defended against possible objections and strengthened by new proofs, by L. Boltzmann [2] and O. E. Meyer.[3]

The object of these speculations was to determine by the method of probabilities the final state of motion which must obtain in a very large number of gaseous molecules after a long lapse of time, supposing the gas left at rest and protected from the action of external forces.

In this state the molecules cannot all possess one and the same velocity. From the collisions taking place in widely different directions, they must, on the contrary, acquire very different values, some of which are greater and others less than the given mean value u. Many of these values will occur frequently, others but rarely.

Maxwell's speculation has for its object the determination of the relative frequency of each possible value of the velocity in the final state of motion assumed after a large number of collisions between the particles.

This final state of equilibrium is characterised by the fact that under all possible conditions it is the one which is most probable to result, and, when once produced, has the greatest likelihood of continuing.

It can be determined without a knowledge of the laws which govern the impact of molecules, merely by the aid of

[1] *Phil. Mag.* [4], 1860, xix. p. 22; 1868, xxxv. p. 185.

[2] *Wien. Akad. Sitz.-Ber.* 1868, lviii. p. 517; 1871, lxiii. pp. 397 and 679; 1872, lxvi. p. 275.

[3] *Die kinetische Theorie der Gase*, chap. ii. 259. Breslau, 1877.

very general axioms of mechanics, especially by the law of the conservation of energy.

The only assumption made is that no energy is lost by the impact of the particles, and that the particles exercise no influence of any kind on each other except during the very short time of contact. It is also considered that in the case of a polyatomic molecule, *i.e.* a molecule composed of several atoms, the motion of the molecule may be partly or entirely converted into motion of the individual atoms, and, inversely, motion of the individual atoms may be converted into that of a molecule. Further, it may also happen that the molecules are dissimilar in nature, and consequently belong to different gases.

Starting from this basis it is possible to determine the arithmetical mean value of the velocity Ω, which is expressed by the equation—

$$p = \frac{\pi}{8} n \cdot \mathfrak{M} \Omega^2,$$

and consequently bears the following relation to the mean value of Clausius:

$$\Omega = \mathfrak{u} \sqrt{\frac{8}{3\pi}} = 0{\cdot}9213\ \mathfrak{u}.$$

The different velocities which really occur differ from the mean value according to the laws discovered by Maxwell in the same way that measurements affected by errors of observation differ from the correct value of the measured quantity.

In each case the mathematical law holds good which Gauss has employed in the theory of the method of least squares. Great deviations from the mean are rare, small deviations are more frequent; so that the statement that all velocities are nearly equal does not deviate far from the truth.

By the aid of this law of Maxwell's, the relative frequency of any one of the many possible values of the molecular velocity can be calculated, and consequently the relative frequency of each definite value of the kinetic energy of the

progressive motion can also be calculated. This calculation proves that in a mixture of several gases the probability of a certain value of the energy for the molecules of a particular gas is just as great as for the molecules of any other gas. Although the idea previously mentioned, that, in a mixture of several gases, the molecules of one gas may possess double, treble, or only half or a third the energy of the others, appears *à priori* probable, it is nevertheless entirely improbable. Consequently the number of molecules in equal volumes of different gases must, according to the law of probabilities, be equal under similar conditions of temperature and pressure.

In this way Avogadro's hypothesis attains the same degree of probability which the kinetic theory of gases has obtained. Avogadro's hypothesis must remain indispensable, whatever views may be held regarding the nature of the gaseous state.

Important objections have never been raised to this hypothesis. Whenever it has been discussed the discussion has merely related to the question of the convenience of accepting the hypothesis.[1] Its correctness has never been disputed.

Since this hypothesis alone preserves a uniform agreement between chemical and physical theories, its recognition can no longer be denied[2] in the present condition of the science, and must, therefore, now be universally acknowledged.

§ 16. It is not possible to determine the absolute magnitude of the molecular weights by means of the hypothesis that equal volumes of different gases contain an equal number of molecules, but the relative magnitudes of the molecular weights of all bodies, the density of which in the gaseous state has been measured, may be determined. The molecular weights are proportional to the densities. Hydrogen gas has been conveniently chosen as the standard, since it has the smallest density and consequently the smallest molecular weight. Hence the chemists who have accepted this hypothesis agree that the weight of a molecule of hydrogen, which, according to the

[1] Berzelius, *Lehrb.* 5. Aufl. i. p. 62.

[2] Ampère, *loc. cit.* p. 47.

statements in § 8 contains at least two atoms, shall be represented as equal to two.

But as Avogadro took the molecule and not the atom of hydrogen as unity, the numbers at present used for the molecular weights are double those he proposed.[1]

The molecular weight of any other gas can be easily ascertained as soon as its density is known, the former, according to the hypothesis, being proportional to its density. Let d be the density of the gas (compared with air), of which the molecular weight $\mathfrak{M}$ is required; since the density of hydrogen compared with air = 0·06926,[2] and its molecular weight $\mathfrak{H} = 2$; then—

$$\mathfrak{M} : \mathfrak{H} = \mathfrak{M} : 2 = d : 0{\cdot}06926,$$

and

$$\mathfrak{M} = \frac{2 \,.\, d}{0{\cdot}06926} = 28{\cdot}877d.$$

Since it may appear doubtful whether the density of hydrogen can be determined with the same degree of accuracy as denser gases, *e.g.* oxygen, it has been proposed first to determine the relation of the required molecular weight to that of oxygen, and then to express this number in terms of hydrogen as unity.[3]

The density of oxygen compared with air is, according to Regnault,[4] 1·10563. Let $\mathfrak{O}$ represent its molecular weight, then

$$\mathfrak{M} : \mathfrak{O} = d : 1{\cdot}10563,$$

and

$$\mathfrak{M} = \frac{\mathfrak{O} \,.\, d}{1{\cdot}10563}.$$

[1] Recently certain authors have again commenced to make use of Avogadro's numbers, and to regard as molecular weights the numbers obtained when hydrogen instead of air is taken as the unit of density. But so long as the atom of hydrogen = 1 and not 0·5, as Avogadro assumed, this arrangement is inconvenient and purposeless, since the molecular weight will no longer represent the sum of the weights of all the atoms contained in the molecule.

[2] See Regnault, *Relation des Expériences*, &c., i. 1847, p. 143.

[3] Bödeker, *Die gesetzmässigen Beziehungen zwischen Zusammensetzung, Dichtigkeit und spec. Wärme der Gase.* Göttingen, 1857. Bödeker takes Avogadro's unit and represents the corresponding calculated numbers expressed in decigrammes of 1119·05 cbc of different gases. This is, however, an unnecessary complication, since the numbers calculated from the above equation are quite independent of every standard of measure and weight.

[4] Regnault, *loc. cit.* p. 143.

According to Avogadro's speculation (§ 8) on the composition of water, a molecule of this compound contains half a molecule of oxygen and a whole molecule of hydrogen. According to the determinations of Dumas[1] and Stas,[2] water contains 15·96 parts by weight of oxygen to two parts by weight (*i.e.* one molecule) of hydrogen. Hence it follows that—

$$\mathfrak{O} : \mathfrak{H} = 31{\cdot}92 : 2, \text{ or } \mathfrak{O} = 31{\cdot}92,$$

and

$$\mathfrak{M} = \frac{31{\cdot}92.d}{1{\cdot}10563} = 28{\cdot}864d,$$

which nearly agrees with the number previously obtained.

In the following pages the mean of these two numbers, $\mathfrak{M} = 28{\cdot}87 \,.\, d$, will be used in calculating molecular weights.

§ 17. The molecular weight must be either equal to the atomic weight or to a simple multiple of it, since molecules must consist of a finite number of whole atoms and cannot contain any fractions of the atoms, which are regarded as indivisible. The atomic weight of an element is not known in the first instance, but only its combining weight or its stochiometric value, that is, the quantity of the given element which unites with a definite quantity of another element selected as unity. This combining weight must, however, be either equal to the atomic weight or be a simple multiple or sub-multiple of the atomic weight, since combination of the elements only takes place between whole atoms. Hence the molecular weight and the combining weight must either be equal or bear a simple relation to each other.

When this is not the case, it is probable that either the vapour density or the combining weight, or that both, have been incorrectly determined. In most cases the quantitative determination is more exact than the measurement of the vapour density. When this is believed to be the case, the molecular weight is considered to be equal to that multiple of the combining weight which approximates to the value calculated from the density.

For example, a former determination of the density of

[1] *Compt. Rend.* 1842, xiv. p. 537; *Ann. Chim. Phys.* [3], 1843, viii. p. 200.

[2] *Nouvelles Recherches sur les Lois des Proportions Chimiques*, &c. Bruxelles, 1865, p. 24.

chlorine gas by Regnault gives 2·440 compared with atmospheric air as unity.

By multiplying this number by the coefficient 28·87, the molecular weight of chlorine is found to be 70·44. But, according to the very exact analytical determinations of Stas, the combining weight of chlorine = 35·37 when H = 1. 70·74, which is double this number, agrees closely with the molecular weight calculated from the density, and is consequently regarded as the correct relative weight of the molecule, since the analytical determination is in this case much more exact than the determination of the density. E. Ludwig's determination[1] of the density of chlorine gas at 200° C. = 2·450 corresponds to the molecular weight 70·73, which coincides with the stochiometric number. But the lack of agreement between the value for the molecular weight calculated from the density and the stochiometric quantity can also arise from another cause than the inexactitude of the determinations. Gay-Lussac's law (§ 5), that the volumes of gas entering into a mutual reaction are either equal or bear a simple relation to each other, is only true within certain limits. It is only perfectly true within certain special limits of temperature and pressure peculiar to each kind of gas. This follows as a natural consequence from the observation that different gases do not undergo precisely the same alteration of volume for similar changes of temperature and pressure. Boyle's law, that the volume of a gas is inversely proportional to the pressure, and Gay-Lussac's law, that the volume is directly proportional to the absolute temperature, are only approximately true. The coefficients expressing the changes of volume for alterations of temperature and pressure are neither quite independent of the absolute temperature and pressure nor of the chemical nature of the gas. Hence it follows that equal volumes of different gases do not, under all conditions, contain exactly the same number of molecules, and also that the calculation of the molecular weight from the vapour density, which depends on this assumption, can only yield a perfectly exact result under certain fixed conditions. Hence it is generally necessary to correct the molecular weights

[1] *Ber. d. deut. chem. Ges.* 1868, i. 232.

deduced from the density of the gas by those deduced from its quantitative analysis.

The necessity of this correction has the advantage of rendering it superfluous to make an accurate determination of the vapour density for calculating the molecular weight.

Even a merely approximate determination of the density is sufficient for calculating the molecular weight when the combining weight is accurately known.

Although it is perfectly obvious, it is, however, not unworthy of mention that the above method of calculating the molecular weight can only be applied to homogeneous gases. In the case of a gaseous mixture it would merely give the mean value of the heterogeneous molecules contained in the mixture.

§ 18. The density in the gaseous state is only known for a few elements, since many elements are only volatile at very high temperatures, at which our methods of experimentally determining the density of gases can no longer be employed. Only about one-fifth of all the known elements are volatile at moderate or not very high temperatures. The following table containing these elements gives under d the density observed by the experimentalists in column III. at the temperature t (column IV.). Column V. contains the product 28·87 into d; that is, the molecular weight calculated directly from the density. And column VI. contains the molecular weight $\mathfrak{M}$ corrected by means of the stochiometric values.

In accordance with Cannizzaro's suggestion,[1] the latter are represented by Gothic capitals. The temperatures for Mitscherlich's observations have been calculated by the author from Mitscherlich's data. (See table on next page.)

The behaviour of sulphur, as seen from this table, is very striking. Two different molecular weights are obtained for sulphur, according to the temperature at which the observations are made. The value obtained at temperatures above 800° C. is only one-third of that found by Dumas at 524°, and by Mitscherlich at 508°. $\mathfrak{S}' = 3 \cdot \mathfrak{S}$; *i.e.* (assuming the observations to be correct) the molecule of sulphur existing at 500° decomposes into three parts whenever its temperature is

[1] S. Cannizzaro, *Sunto di un corso di filosofia chimica*. Pisa 1858, p. 15. *Nuovo Cimento*, vol. vii. 1858.)

I.	II. Density. d	III. Obs.	IV. t	V. $28{\cdot}87 \cdot d$	VI. $\mathfrak{M}$
Hydrogen . .	0·06926	Rg	0° C.	2	$\mathfrak{H}$ = 2
Nitrogen . .	0·9713	,,	0°	28·04	$\mathfrak{N}$ = 28·02
Oxygen . .	1·10563	,,	0°	31·92	$\mathfrak{O}$ = 31·92
Sulphur . .	2·23	DT	746°	64·4	$\mathfrak{S}$ = 63·96
,, . .	2·24	,,	940°	64·6	,, = ,,
,, . .	2·17	VM	1,400° *cir.*	62·7	,, = ,,
,, . .	6·62	Ds	524°	191·1	$\mathfrak{S}'$ = 191·88
,, . .	6·90	M	508°	199·2	,, = ,,
Chlorine . .	2·450	L	200°	70·73	$\mathfrak{Cl}$ = 70·74
,, . .	2·44	VM	620°	70·45	,, = ,,
Cadmium . .	3·94	DT	940°	113·7	$\mathfrak{Cd}$ = 111·7
Phosphorus .	4·35	Ds	500°	125·6	$\mathfrak{P}$ = 123·84
,, . .	4·58	M	515°	132·2	,, = ,,
,, . .	4·50	DT	940°	129·9	,, = ,,
Bromine . .	5·54	M	100°	159·9	$\mathfrak{Br}$ = 159·52
,, . .	5·52	J	228°	159·4	,, = ,,
Selenium . .	5·68	DT	1,420°	161·1	$\mathfrak{Se}$ = 157·74
Mercury . .	6·98	Ds	446°	201·5	$\mathfrak{Hg}$ = 199·8
,, . .	7·03	M	424°	203·0	,, = ,,
,, . .	6·86	VM	440°	198·1	,, = ,,
,, . .	6·81	,,	1,400° *cir.*	196·3	,, = ,,
Iodine . .	8·72	Ds	185°	251·7	$\mathfrak{J}$ = 253·06
,, . .	8·70	DT	447°	251·2	,, = ,,
,, . .	8·72	,,	1,040°	251·7	,, = ,,
Tellurium . .	9·00	,,	1,440°	259·8	$\mathfrak{Te}$ = 252·3
,, . .	9·08	,,	1,390°	262·1	,, = ,,
Arsenic . .	10·65	M	644—668°	307·4	$\mathfrak{As}$ = 299·6
,, . .	10·2	DT	746°	294·5	,, = ,,
Zinc . .	2·36	VM	1,400° *cir.*	68·1	$\mathfrak{Zn}$ = 65

In column III. the following abbreviations are used:—Rg, Regnault, 1847; Ds, Dumas, 1826 and 1832; M, Mitscherlich, 1833; DT, Deville and Troost, 1859 and 1863; L, E. Ludwig, 1868; VM, Victor Meyer, 1879 and 1886; J, H. Jahn, 1852.

raised considerably above this point. This molecule appears, therefore, to be a comparatively easily variable value. Whether the decomposition takes place suddenly at a definite temperature or gradually has not yet been ascertained with certainty. Bineau[1] has indeed published observations according to which sulphur vapour possesses the following densities between 700° and 1,200°:—

Temperature .	714°	727°	731°	743°	Mean.
Density . .	2·8	2·7	2·6	2·8	2·7°
Temperature .	834°	851°	963°	1082°	1162°
Density . .	2·4	2·6	2·4	2·1	2·3

[1] *Compt. Rend.* 1859, xlix. p. 799. *Lieb. Ann.* 1860, cxiv. s. 383.

But the experimental method he employed is by no means accurate.[1] The results are doubtful. But the experiments of Deville and Troost on selenium render it probable that the numbers obtained by Bineau for sulphur are not very incorrect.

The density of selenium vapour compared with air at the same temperature and pressure is not constant. It decreases with an increase in temperature. At 1420° the density gives 161 as the molecular weight, which corresponds to the value 157·7 obtained by quantitative analysis. Hence at this temperature selenium vapour appears to consist essentially of molecules, having the weight Se = 156, with which, however, a certain number of larger molecules are mixed. The number of the large molecules must have increased considerably at the somewhat lower temperature of 940°, and at 746° the number is again greater, since the densities determined at these temperatures give values for the molecular weight, which do not correspond to any stochiometric quantity.

The same is true of chlorine, bromine, and iodine. The numbers in the table only represent the molecular weights of these elements below certain definite limits of temperature. Above these limits smaller values are obtained, which do not exactly correspond to any stochiometric quantities. These exceptions will be discussed in another chapter.

At certain temperatures, therefore, Avogadro's law cannot be employed for the determination of the molecular weights of these elements. It can only be applied where the density of the vapour, compared with the density of air or of another gas, does not vary with the temperature, or is constant within a large interval of temperature. (See §§ 28–34; also section XII.)

This shows how fruitless was the attempt which was frequently made to assign values to the atomic weights (which are theoretically immutable), which should be proportional to the above molecular weights, and how futile it was to take the density of the gas or vapour as a direct measure of the atomic

[1] See the criticism of H. Sainte-Claire Deville and Troost, *Ann. Chim. Phys.* [3], 1860, lviii., p. 299.

weight, and not, as Avogadro intended, of the molecular weight.

§ 19. Avogadro's hypothesis can only be used indirectly for the determination of the atomic weights; even then it is not perfectly reliable under all circumstances. Its application is based on the notion that according to the atomic theory no molecule can contain fractions of atoms.

The knowledge of the molecular weight of the element in the isolated state is not, as a rule, sufficient for making this determination; it is necessary to know the molecular weight of one or more of its compounds. But this can easily be accomplished by means of Avogadro's hypothesis, which applies not only to elements hitherto undecomposed, but also to all their compounds which can be obtained in the gaseous state (see § 6). According to this hypothesis each gaseous compound contains exactly the same number of molecules in a given volume as the same volume of any of the elements in the gaseous state. Hence we obtain the relative molecular weights of compounds by multiplying their density in the gaseous state, compared with air as unity, by the coefficient 28·87. This product must bear a simple relation to the combining weight, and it may be corrected by the aid of the latter number. For example, according to Biot and Arago, the density of hydrochloric acid gas is 1·247, from which it follows that the molecular weight is $28{\cdot}87 \times 1{\cdot}247 = 36{\cdot}00$, which nearly agrees with the sum of the combining weights of its constituents, as found by analysis, viz. 1 part by weight of hydrogen, and 35·37 parts by weight of chlorine. Hence the corrected molecular weight is 36·37.

According to Regnault's determination, the density of steam at 100° C. = 0·623, and the molecular weight = $28{\cdot}87 \times 0{\cdot}623 = 17{\cdot}99$. One part of hydrogen unites with 7·98 parts of oxygen to form water. The sum $1 + 7{\cdot}98 = 8{\cdot}98$ is nearly equal to half the molecular weight calculated from the density. The corrected molecular weight is therefore $2 \times 8{\cdot}98 = 17{\cdot}96$, and this molecule contains 2 parts by weight of hydrogen, and 15·96 parts by weight of oxygen.

The calculation is scarcely less simple if the compound does not contain any hydrogen. Berzelius found that the

anhydride of sulphurous acid, composed of sulphur and oxygen, has the density 2·247, which corresponds to the molecular weight 28·87 × 2·247 = 64·87. But quantitative analysis shows that 64·87 parts by weight of this compound contain 32·40 parts by weight of oxygen, and 32·47 parts by weight of sulphur. The combining weights of each of these elements, *i.e.* the quantities which combine with one part by weight of hydrogen, are 7·98 for oxygen, and 15·99 for sulphur. These weights should stand in a simple relation to the previous values, which is not exactly the case. But the multiples 4 × 7·98 = 31·92, and 2 × 15·99 = 31·98 approximate those of the uncorrected molecular weights 32·40 and 32·47 so closely that we have no hesitation in accepting the former as correct.

The molecular weight of sulphurous anhydride is therefore assumed to be 31·92 + 31·98 = 63·90, instead of 64·87.

§ 20. The stochiometric numbers can not only be used for correcting the molecular weight calculated from the vapour density determinations, but they can also, under certain circumstances, be employed for calculating the molecular weight when the density cannot be correctly determined. It is only necessary to observe how many volumes of one or other of the constituents are contained in a volume of the gaseous compound, or how many volumes of one or the other products of decomposition can be obtained from one volume of the compound. The densities of the hydrides of selenium and tellurium have not been directly determined; but the experiments of Bineau [1] show that both gases, when brought in contact with certain metals, deposit all their selenium and tellurium, leaving a volume of hydrogen equal to that of the original gas. It follows from these experiments that each particle of selenium or tellurium hydride contains exactly the same quantity of hydrogen as a molecule of free hydrogen contains, viz. two atoms (see § 8).

But the analytical determinations show that selenium hydride contains 39·43 parts by weight of selenium to 1 of hydrogen, and that tellurium hydride contains 63 parts by weight of tellurium to 1 part by weight of hydrogen. Hence

[1] Gmelin's *Handb. d. Chemie*, 5. Aufl. i. 684, ii. 804.

the molecular weights of these compounds contain double these quantities. Thus the molecule of selenium hydride consists of 2 parts by weight of hydrogen and 78·87 parts by weight of selenium, and tellurium hydride contains 2 parts by weight of hydrogen and 126 parts by weight of tellurium.

The molecular weights of these compounds are therefore $2 + 78{\cdot}87 = 80{\cdot}87$, and $2 + 126 = 128$, from which the densities may be calculated.

For selenium hydride $d = \frac{80{\cdot}87}{28{\cdot}87} = 2{\cdot}80$, and for tellurium hydride $d = \frac{128}{28{\cdot}87} = 4{\cdot}43$, compared with air under similar conditions of temperature and pressure.

Similarly the molecular weight and density of hydrobromic acid can be deduced from the two observations, first, that this gas contains 79·76 parts by weight of bromine to one part by weight of hydrogen, and, secondly, that when the bromine is removed by metals or other substances, the hydrogen which remains [1] occupies exactly half the volume of the original gas.

Hence the molecule of hydrobromic acid contains half a molecule, *i.e.* one atom of hydrogen and 79·76 parts by weight of bromine.

§ 21. From the molecular weights of compounds, determined directly or indirectly by the above methods, and corrected by means of analytical experiments, the atomic weights of the constituents may be deduced. Since an atom is defined as that quantity which cannot be further split up by chemical decomposition, it follows that no molecule of a compound can contain fractions of atoms. Therefore that quantity of an element which is found in the molecular weight of one of its compounds must represent at least one atomic weight, but it may represent two or more atomic weights. It can only be equal to the atomic weight itself, or a simple multiple of the same, and it can never represent a fraction of an atom. Let Q be the quantity contained in a molecule, and A the atomic weight; then $Q = n \cdot A$, and $A = \frac{1}{n} \cdot Q$, where the unknown factor n represents a whole number, *e.g.* $n = 1, 2, 3, 4$, &c.

[1] Balard, *Ann. Chim. Phys.* 1826, xxxii. p. 350.

$A = Q$ when $n = 1$, and this is the maximum value which can be assigned to the atomic weight.

This process does not fix the atomic weight, but is an important step towards so doing, since it excludes a number of possible values for the same. For example, the molecular weight of silicon chloride, as calculated from the vapour density (5·94) and corrected by analytical experiments, is 169·5, viz., 28 parts of silicon and 141·5 parts by weight of chlorine. Hence the atomic weight of silicon can only possess one of the following values:

$$\text{Si} = 28\text{; or } \frac{28}{2} = 14\text{; or } \frac{28}{3} = 9{\cdot}33\text{; or } \frac{28}{4} = 7\text{, \&c.}$$

The value which was formerly accepted as the atomic weight of silicon, Si=21, is therefore excluded, as in this case the molecule of the chloride would contain $\frac{4}{3}$ of an atom. But whether the atomic weight be 28 or 14 remains undecided.

The choice of the possible values for the atomic weight is further limited by comparing several compounds of the same element.

It is obvious that the quantity of chlorine (141·5) contained in a molecule of silicon chloride consists of more than one atom, as compounds are known to exist which contain a smaller quantity of chlorine.

The molecular weight of liquid chloride of phosphorus = 137, containing 106·1 parts of chlorine; that of corrosive sublimate = 270·5, containing 70·74 parts of chlorine; and the molecular weight of hydrochloric acid = 36·37, containing 35·37 parts by weight of chlorine. These amounts of chlorine are in the proportion 4 : 3 : 2 : 1, *i.e.*—

$$141{\cdot}5 = 4 \times 35{\cdot}37\text{; } 106{\cdot}1 = 3 \times 35{\cdot}37\text{; } 70{\cdot}74 = 2 \times 35{\cdot}37.$$

The atomic weight of chlorine is therefore limited to 35·37, or to the half, third, quarter, or fifth of this number.

Not one of the numerous compounds of chlorine of which the molecular weight has been calculated from the vapour density determination is known to contain less than 35·37 parts of chlorine[1] in a molecule—*i.e.* contains less chlorine

[1] The apparent exception in the case of ammonium chloride and similar compounds is discussed in §§ 30 and 31.

in the gaseous state than is contained in an equal volume of hydrochloric acid gas. But since, on the other hand, all these compounds contain either exactly this quantity or a simple multiple of it, it is very probable that the atomic weight of chlorine is 35·37, and not half, or a third, or any other fraction of this number. But this does not prove the assumption to be correct.

§ 22. If a single gaseous compound was known which contained only half as much chlorine or hydrogen as is contained in the same volume of hydrochloric acid gas,[1] it would be necessary to take the atomic weight as half the above number.

$$H = 0{\cdot}5 \qquad \text{and } Cl = 17{\cdot}685,$$
$$\text{and } \mathfrak{H} = H_4 = 2, \text{ and } \mathfrak{Cl} = Cl_4 = 70{\cdot}74\ ;$$

or, if the atomic weight of hydrogen is taken as unity, then

$$H = 1 \qquad \text{and } Cl = 35{\cdot}37,$$
$$\mathfrak{H} = H_4 = 4, \text{ and } \mathfrak{Cl} = Cl_4 = 141{\cdot}48.$$

In the case of hydrogen gas this would agree with Ampère's view, according to which a molecule ('particule') contains at least four atoms ('molécules'). The hope of arriving at a knowledge of Hauy's crystallographic elements, the so-called 'molécules intégrantes,' induced him to adopt the theory that a molecule is composed of at least four atoms. He imagined that the four atoms are arranged like the angles of a tetrahedron, and he regarded the tetrahedral space so bounded as the desired 'molécule intégrante.' This speculation has, so far, borne no results, and therefore does not appear justifiable. All known facts appear to prove that the molecule of free hydrogen can never be divided into more than two parts; consequently, the half molecule must be regarded as an atom, and the molecule as a compound of two atoms. H. Davy's experiments on the so-called 'euchlorine' led Ampère to believe that the molecule of chlorine contains eight atoms. This view has proved equally unjustifiable.

But similar hypotheses regarding phosphorus and arsenic are received as correct. The existence of at least four atoms

[1] Some authors have assumed this to be the case for ammonium chloride (see §§ 30, 31).

in their molecules must be assumed, since compounds exist which contain, in the gaseous state, only a quarter of the quantity of arsenic or phosphorus which is found in the same volume of the free element in the gaseous state.

In the above cases the most probable value of the atomic weight is the smallest quantity of an element which occurs in the molecular weight of any of its compounds. Hence it is clearly important, for the determination of the atomic weight, to obtain a knowledge of the molecular weight especially of those compounds which contain the smallest proportion by volume of the given element. In many cases the atomic weight can be deduced from those compounds, which undoubtedly contain more than a single atom in the molecule.

The maximum value for the atomic weight of fluorine deduced from the molecular weight of methyl fluoride, viz., 34·03, which contains 19·06 parts by weight of fluorine, can also be obtained by a comparison of the molecular weight of boron fluoride, viz., 68·08, containing 57·18 parts by weight of fluorine, with the molecular weight of silicon fluoride, viz., 104·24, containing 76·24 parts by weight of fluorine. Since the molecule of each of these compounds can only be composed of whole atoms, the difference between the quantities of fluorine contained in both molecules must represent at least one whole atomic weight. This difference, viz., $76{\cdot}24 - 57{\cdot}18 = 19{\cdot}06$, is equal to the quantity contained in the molecular weight of methyl fluoride.

Since the quantities contained in both the other compounds are simple multiples of this number, viz., $57{\cdot}18 = 3 \times 19{\cdot}06$ and $76{\cdot}24 = 4 \times 19{\cdot}06$, the atomic weight of fluorine is taken as 19·06, and boron fluoride and silicon fluoride are assumed to contain respectively three and four atoms of fluorine in the molecule.

The rule for deducing the atomic weight from the molecular weight may in general be expressed thus: the atomic weight of an element must be so determined that the molecular weights of all its compounds contain the element in quantities which are simple multiples of its atomic weight.

This value may be too high, but can never be too low, provided the experimental results be correct. If it is not the

correct value of one atom, it will represent 2, 3, 4, or any other number of whole atoms; how many atoms it corresponds to cannot be decided offhand.

Although the knowledge of the density of the gas or vapour, and of the molecular weight deduced therefrom, is very valuable, it is nevertheless not a thoroughly sufficient means of determining the atomic weight. It only gives the maximum value which can be assigned to the atomic weight, but does not decide whether the atomic weight is in reality a simple or sub-multiple of that maximum. But where the number of investigated compounds is very large, as is the case for carbon, hydrogen, nitrogen, and other elements, the probability is very great that the smallest quantity of the element found in any molecule is in reality the smallest quantity which can be present, and that this smallest quantity is the atomic weight itself, and not a multiple of this number. Although it is not impossible, it is very improbable, that in the investigation of a large number of the compounds of an element, not one should be met with containing only one single atom of this element. But where the density in the gaseous state, and consequently the molecular weight, of only one or two of the compounds of an element has been determined, the conclusions deduced as to the atomic weight are generally doubtful, and consequently require confirmation by other methods.

§ 23. The following table gives the densities of a large number of compounds and the molecular weights deduced from them, these compounds fulfilling the conditions mentioned above for determining the atomic weights; that is, they contain the smallest quantity of the given element in the unit of volume.

All the elements of whose compounds the vapour density has been determined are contained in this table. Elements which form many such compounds are represented only by a selection from them.

Amongst these substances are placed the compounds of those elements which are not found in the table, § 16, because their molecular weights in the isolated or so-called free state are not known. It is obvious that the knowledge of the density in the free state is not required in determining the

atomic weight. The first column of the table contains the names of the compounds; the second, under *d*, the density compared with air; the third, the abbreviation of the name of the investigator; the fourth, under 28·87 *d*, the uncorrected molecular weight in round numbers; the fifth, under $\mathfrak{M}$, the molecular weight corrected from analytical results; finally, the sixth shows the quantities of the constituents contained in the molecule; *i.e.* the amount contained by the compound in the gaseous state, in a volume equal to that occupied by two parts by weight of hydrogen under similar conditions of temperature and pressure. The following abbreviations are used for the names of the investigators: B. A., Biot and Arago; Ba., Balard; Bé., Bérard; Bi., Bineau; Bk., Buckton; Bn., Bunsen; Bt., Butlerow; Bz., Berzelius; Ch., Cahours; Col., Colin; Db., Debray; D. Db., Deville and Debray; Ds., Dumas; Ds. P., Dumas and Peligot; D. T., Deville and Troost; Dv., John Davy; E. L., Emmerling and Lengyel; Fd., Friedel; Fd. C., Friedel and Crafts; Fk., Frankland; G.-L., Gay-Lussac; Hf., A. W. Hofmann; Jq., Jacquelin; Kb., Kolbe; L. B., Lecoq de Boisbaudran; L. S., Löwig and Schweitzer; Mt., Mitscherlich; Rc., Roscoe; Rg., Regnault; Rs., Rose; Sl., Salet; T. H., Troost and Hautefeuille; Tm., Thompson; Tn., Than; Tp., Thorpe; V. M., Victor Meyer; W. D., Wöhler and Deville; Wd., Wrede; Wk., Wanklyn; Wt., Walter; Wz., Würtz; Z., Zimmermann.

VAPOUR DENSITIES AND MOLECULAR WEIGHTS.

	d.	Observ.	28·87*d*	$\mathfrak{M}$	CONSTITUENTS	
					Parts by Weight of	
Hydrofluoric acid .	—	Gore	—	20·06[1]	1·0	hydrogen
					19·06	fluorine
Hydrochloric acid .	1·247	B. A.	36·0	36·37	1·0	hydrogen
					35·37	chlorine
Hydrobromic acid .	—	Ba	—	80·76	1·0	hydrogen
					79·76	bromine
Hydriodic acid . .	4·443	G. L.	128·0	127·53	1·0	hydrogen
					126·53	iodine
Water . .	0·623	Rg	17·99	17·96	15·96	oxygen
	0·623	D. T.	17·99	17·96	2·0	hydrogen

[1] Determined indirectly; see § 20, p. 31. According to Mallet (*Amer. Chem. Journ.* 1881, iii. 189), the molecular weight should be double.

VAPOUR DENSITIES AND MOLECULAR WEIGHTS—*continued.*

	d.	Observ.	28·87*d*	M	Constituents: Parts by Weight of	
Sulphuretted hydrogen	1·191	G. L.	34·4	33·98	**31·98**	sulphur
					2·0	hydrogen
Sulphur dioxide	2·247	Bz	64·9	63·90	**31·98**	sulphur
					31·92	oxygen
Sulphur trioxide	3·01	Mt	86·9	79·86	**31·98**	sulphur
					47·88	oxygen
Sulphuryl chloride	4·67	Rg.	134·8	134·64	**31·98**	sulphur
					31·92	oxygen
					70·74	chlorine
Selenium hydride	—	Bi.	—	80·87[1]	**78·87**	selenium
					2·0	hydrogen
Selenium dioxide	4·03	Mt.	116·0	111·79	**78·87**	selenium
					31·92	oxygen
Tellurium hydride	—	Bi.	—	128·3[2]	**126·3**	tellurium
					2·0	hydrogen
Ammonia	0·597	BA.	17·2	17·01	**14·01**	nitrogen
					3·0	hydrogen
Nitric oxide	1·039	Bé.	30·0	29·97	**14·01**	nitrogen
					15·96	oxygen
Nitrous oxide	1·520	Col.	43·9	43·98	**15·96**	oxygen
					28·02	nitrogen
Phosphorus hydride	1·15	Rs.	33·1	33·96	**30·96**	phosphorus
					3·0	hydrogen
Phosphorus pentafluoride	—	Tp.	—	126·26	**30·96**	phosphorus
					95·3	fluorine
Phosphorous chloride	4·88	Ds.	140·9	137·07	**30·96**	phosphorus
					106·11	chlorine
Phosphorus oxychloride	5·40	Wz.	155·9	153·03	**30·96**	phosphorus
					15·96	oxygen
					106·11	chlorine
Phosphorus sulphochloride	5·88	Ch.	169·7	169·05	**30·96**	phosphorus
					31·98	sulphur
					106·11	chlorine
Triethyl phosphine oxide	4·60	Hf.	132·8	133·74	**30·96**	phosphorus
					15·96	oxygen
					71·82	carbon
					15·0	hydrogen
Arseniuretted hydrogen	2·695	Ds.	77·8	77·9	**74·9**	arsenic
					3·0	hydrogen
Arsenious chloride	6·30	Ds.	181·9	181·0	**74·9**	arsenic
					106·11	chlorine
Cacodyl chloride	4·56	Bn.	131·7	140·2	**74·9**	arsenic
					35·37	chlorine
					23·94	carbon
					6·0	hydrogen
Cacodyl cyanide	4·63	Bn.	133·7	130·8	**74·9**	arsenic
					14·01	nitrogen
					35·91	carbon
					6·0	hydrogen
Arsenic tri-iodide	16·1	Mt.	464·8	454·5	**74·9**	arsenic
					379·59	iodine

[1] Indirect determination. See § 20.

[2] Density not given. *Chem. News*, 1875, xxxii. 232.

VAPOUR DENSITIES AND MOLECULAR WEIGHTS—*continued.*

	d.	Observ.	28·87*d*	M	CONSTITUENTS Parts by Weight of	
Antimony trichloride	7·8	Mt.	224·7	226·1	120·0	antimony
					106·11	chlorine
Antimony triethide	7·44	L. S.	214·8	206·8	120·0	antimony
					71·82	carbon
					15·0	hydrogen
Bismuth trichloride	11·35	Jq.	327·7	313·6	207·5	bismuth
					106·11	chlorine
Boron trifluoride	2·312	Ds.	66·8	68·1	10·9	boron
					57·18	fluorine
Boron trichloride	3·942	Ds.	113·8	117·0	10·9	boron
	4·02	W. D.	116·1	117·0	106·11	chlorine
Boron tribromide	8·78	W. D.	253·5	250·2	10·9	boron
					239·25	bromine
Boron trimethide	1·93	Fk.	55·7	55·8	10·9	boron
					35·91	carbon
					9·0	hydrogen
Indium chloride	7·78	V. M.	224·7	219·5	113·4	indium
					106·1	chlorine
Marsh gas	0·555	Tm.	16·0	15·97	11·97	carbon
					4·0	hydrogen
Methyl fluoride	1·186	Ds. P.	34·3	34·03	11·97	carbon
					19·06	fluorine
					3·0	hydrogen
Methyl chloride	1·736	Ds. P.	50·1	50·34	11·97	carbon
					35·37	chlorine
					3·0	hydrogen
Methyl bromide	3·253	Bn.	93·9	94·73	11·97	carbon
					79·76	bromine
					3·0	hydrogen
Methyl iodide	4·883	Ds. P.	141·0	141·50	11·97	carbon
					126·53	iodine
					3·0	hydrogen
Chloroform	4·20	Ds.	121·3	119·08	11·97	carbon
					1·0	hydrogen
					106·11	chlorine
Carbon tetrachloride	5·24	Kb.	151·3	153·45	11·97	carbon
	5·33	Rg.	153·9	153·45	141·48	chlorine
Carbon monoxide	0·968	Wd.	27·96	27·93	11·97	carbon
					15·96	oxygen
Carbon dioxide	1·529	Rg.	44·15	43·89	11·97	carbon
					31·92	oxygen
Carbon oxychloride	3·505	E. L.	101·2	98·67	11·97	carbon
					15·96	oxygen
					70·74	chlorine
Carbon oxysulphide	2·105	Tn.	60·8	59·91	11·97	carbon
					15·96	oxygen
					31·98	sulphur
Carbon bisulphide	2·645	G. L.	76·4	75·93	11·97	carbon
					63·96	sulphur
Hydrocyanic acid	0·948	G. L.	27·4	26·98	11·97	carbon
					14·01	nitrogen
					1·0	hydrogen

VAPOUR DENSITIES AND MOLECULAR WEIGHTS—*continued*.

	d.	Observ.	28·874	M	Constituents: Parts by Weight of	
Cyanogen chloride	2·13	Sl.	61·5	61·35	11·97	carbon
					14·01	nitrogen
					35·37	chlorine
Cyanic acid	1·50	T. H.	43·3	42·94	11·97	carbon
					14·01	nitrogen
					15·96	oxygen
Methyl alcohol	1·12	Ds. P.	32·3	31·93	11·97	carbon
					15·96	oxygen
					4·0	hydrogen
Methyl nitrate	2·64	Ds. P.	76·2	76·86	11·97	carbon
					14·01	nitrogen
					3·0	hydrogen
					47·88	oxygen
Silicon fluoride	3·57	Dv.	103·0	104·24	28·0	silicon
					76·24	fluorine
Silicon chloride	5·94	Ds.	171·5	169·5	28·0	silicon
					141·48	chlorine
Silicon iodide	19·1	Fd.	551·4	534·1	28·0	silicon
					506·12	iodine
Silicon ethide	5·13	Fd. C.	148·1	143·8	28·0	silicon
					95·76	carbon
					20·0	hydrogen
Titanium chloride	6·84	Ds.	197·5	189·5	48·0	titanium
					141·48	chlorine
Zirconium chloride	8·15	D. T.	235·4	231·88	90·4	zirconium
					141·48	chlorine
Stannic chloride	9·20	Ds.	265·7	258·83	117·35	tin
					141·48	chlorine
Stannic-ethide	8·02	Fk. Bk.	231·6	233·11	117·35	tin
					95·76	carbon
					20·0	hydrogen
Stannic-triethide chloride	8·43	Ch.	243·4	239·54	117·35	tin
					35·37	chlorine
					71·82	carbon
					15·0	hydrogen
Stannic-triethide bromide	9·92	Ch.	286·4	283·9	117·35	tin
					79·76	bromine
					71·82	carbon
					15·0	hydrogen
Stannic-trimethide iodide	10·33	Ch.	298·2	288·8	117·35	tin
					126·53	iodine
					35·91	carbon
					9·0	hydrogen
Lead chloride	9·5	Rc.	274·3	277·14	206·4	lead
					70·74	chlorine
Lead methide	9·6	Bt.	277·2	266·3	206·4	lead
					47·88	carbon
					12·0	hydrogen
Thallium chloride	8·2	Rc.	236·7	239·07	203·7	thallium
					35·37	chlorine
Zinc chloride	4·57	V. M.	131·9	135·64	64·9	zinc
					70·74	chlorine

VAPOUR DENSITIES AND MOLECULAR WEIGHTS—*continued.*

	d.	Observ.	28·87*d*	M	CONSTITUENTS Parts by Weight of	
Zinc methide	3·29	Wk.	95·0	94·8	64·9	zinc
					23·94	carbon
					6·0	hydrogen
Zinc ethide	4·62	Fk.	123·0	122·8	64·9	zinc
					47·88	carbon
					10·0	hydrogen
Cadmium	3·94	D. T.	113·7	111·7	111·7	cadmium
Cadmium bromide	9·25	V. M.	267·1	271·2	111·7	cadmium
					159·5	bromine
Mercury	6·98	Ds.	201·5	199·8	199·8	mercury
Mercuric chloride	9·8	Mt.	283·0	270·5	199·8	mercury
					70·74	chlorine
Mercuric bromide	12·16	Mt.	351·0	359·3	199·8	mercury
					159·5	bromine
Mercuric iodide	16·2	Mt.	468·0	452·9	199·8	mercury
					253·06	iodine
Mercuric methide	8·29	Bk.	239·4	229·7	199·8	mercury
					23·94	carbon
					6·0	hydrogen
Mercuric ethide	9·97	Bk.	287·8	257·7	199·8	mercury
					47·88	carbon
					10·0	hydrogen
Osmium trioxide	8·9	D. Db.	257·0	262·4 [1]	198·6	osmium
					63·84	oxygen
Chromium oxychloride	5·55	Bi.	159·0	155·1	52·4	chromium
	5·9	Wt.	170·0	—	31·92	oxygen
					70·74	chlorine
Molybdenum pentachloride	9·46	Db.	273·0	272·7	95·9	molybdenum
					176·85	chlorine
Tungsten pentachloride	12·7	Rc.	366·0	360·5	183·6	tungsten
					176·85	chlorine
Tungsten hexachloride	13·2	Rc.	382·0	395·8	183·6	tungsten
					212·22	chlorine
Tungsten oxychloride	11·84	Rc.	342·0	341·0	183·6	tungsten
					15·96	oxygen
					141·48	chlorine
Uranium tetrachloride	13·33	Z.	384·8	381·3	239·8	uranium
					141·48	chlorine
Uranium tetrabromide	19·46	Z.	561·8	558·8	239·8	uranium
					319·04	bromine
Vanadium tetrachloride	6·69 [2]	Rc.	193·0	192·7	51·21	vanadium
					141·48	chlorine
Vanadium oxychloride	6·11	Rc.	176·0	173·3	51·21	vanadium
					15·96	oxygen
					106·11	chlorine
Niobium chloride	9·6	D. T.	277·0	270·6	93·7	niobium
					176·85	chlorine

[1] Probably somewhat lower. See § 5.

[2] In Roscoe's paper in the *Ann. Chem. Pharm.* 1870, vii. Suppl.-Bd. 75, there is a misprint, viz. 6·99 for 6·69.

VAPOUR DENSITIES AND MOLECULAR WEIGHTS—*continued.*

	d.	Observ.	28·87*d*	𝔐	Constituents: Parts by Weight of	
Niobium oxychloride	7·88	D. T.	228·0	215·77	**93·7**	niobium
					15·96	oxygen
					106·11	chlorine
Tantalum chloride	12·9	D. T.	372·0	358·9	**182·0**	tantalum
					176·85	chlorine
Cuprous chloride	7·05	V. M.	203·5	197·0	126·46	copper
					70·74	chlorine
Aluminium chloride	9·35	D. T.	270·0	266·3	54·08	aluminium
					212·22	chlorine
Aluminium bromide	18·6	D. T.	537·0	532·6	54·08	aluminium
					478·5	bromine
Aluminium iodide	27·0	D. T.	780·0	813·26	54·08	aluminium
					759·18	iodine
Ferric chloride	11·39	D. T.	329·0	324·0	111·8	iron
	11·14	V. M.	322·0	324·0	212·22	chlorine
Gallium trichloride						
at 247°	13·4	F.	387·0	352·0	139·8	gallium
at 280°	11·9	L. B.	343·0	„	212·2	chlorine
at 357°	10·5	L. B.	303·0	„	—	—
at 357°	8·5	F.	—	„	—	—
at 447°	7·8	L. B.	—	„	—	—
at 447°	6·6	F.	190·0	„	—	—
Potassium iodide	5·85	V. M.	168·9	165·6	126·5	iodine
					39·1	potassium

The compounds enumerated in this table contain 39 different elements, which is about half the number of the elements at present known.

For some of these compounds, especially for those which are only volatile at high temperatures, there is a large difference between the molecular weights calculated from the observed densities and the corrected numbers. This difference may in many cases arise from impurity or from partial decomposition of the substance, or from an error of experiment.

§ 24. Whether we are justified in regarding the smallest quantity of any of these 39 elements, occurring in their compounds, as the atomic weight, is a question which may be answered in the affirmative, for these elements form a large number of compounds the vapour density of which is known. It is therefore probable that some at least of the compounds are known which contain only one atom of the element in the molecule. This probability is considerably increased by the circumstance that the compounds which contain a small num-

ber of atoms and possess a correspondingly small molecular weight, are, as a rule, more easily volatile, more easily obtained in the gaseous state, and therefore more easily investigated than compounds of the same elements, with a larger number of atoms in the molecule and with a correspondingly higher molecular weight. The probability must not be regarded as a certainty, since the possibility is ever present of another compound being discovered which might contain a smaller quantity of one of these elements in its molecule than had hitherto been observed. This possibility increases when only a small number of the compounds of the given element have been investigated, since in this case it is less certain that there exists amongst the investigated bodies one compound containing only one atom of the element in its molecule.

But the smallest quantity contained in a molecular weight will always be regarded as the atomic weight till reasons are discovered which render it probable or place it beyond doubt that these quantities consist of two, three, or more atoms. Such reasons exist in the case of the elements copper, aluminium, and iron.[1]

The quantity of metal occurring in the molecule of their chlorine, bromine, and iodine compounds can hardly consist of one atom, but in all probability of two. The same conclusion may apparently be drawn in the case of aluminium from the determination of the density of its methyl compound by Buckton and Odling.[2] The density was found to be so small that less than 54·08 parts by weight of aluminium are contained in the molecular weight deduced from this observation. It is, however, probable that the compound was decomposed at the temperature used for its volatilisation, so that the volume occupied by the products of decomposition, and not the volume of aluminium methide, was measured.[3]

With regard to the remaining 33 elements in the table, there is at present no reason why the smallest quantities occurring in the molecular weights should not be regarded as the atomic weights. On the contrary, this assumption is

[1] See § 39. [2] *Lond. Roy. Soc. Proc.* xiv. 19; *Phil. Mag.* [4], xxix. 316.
[3] Williamson, *Roy. Soc. Proc.* xiv. 74; *Phil. Mag.* [4], xxix. 395 A. Wanklyn, *ibid.* p. 313.

strengthened by frequent confirmation, otherwise its value would be but doubtful.

§ 25. A comparison of the atomic weights, determined with the aid of Avogadro's hypothesis from the molecular weights of compounds, with the molecular weights of the elements themselves, so far as these are known, shows that only in the case of mercury, cadmium, and zinc are the atomic and molecular weights identical. In the case of all the other elements the molecular weight is a multiple of the atomic weight.

Element	Atomic Weight	Molecular Weight
Hydrogen	H = 1	H = H_2 = 2
Boron	B = 10·9	B = ?
Carbon	C = 11·97	C = ?
Nitrogen	N = 14·01	N = N_2 = 28·02
Oxygen	O = 15·96	O = O_2 = 31·92
Fluorine	F = 19·06	F = ?
Silicon	Si = 28	Si = ?
Phosphorus	P = 30·96	P = P_4 = 123·84
Sulphur	S = 31·98	S = S_2 = 63·96[1]
		or = S_6 = 191·88[2]
Chlorine	Cl = 35·37	Cl = Cl_2 = 70·74[3]
Titanium	Ti = 48	Ti = ?
Vanadium	V = 51·1	V = ?
Chromium	Cr = 52·45	Cr = ?
Zinc	Zn = 64·9	Zn = Zn = 64·9
Gallium	—	Ga
Arsenic	As = 74·9	As = As_4 = 299·6
Selenium	Se = 78·9	Se = Se_2 = 157·8
Bromine	Br = 79·76	Br = Br_2 = 159·52[3]
Zirconium	Zr = 90·4	Zr = ?
Niobium	Nb = 93·7	Nb = ?
Molybdenum	Mo = 95·9	Mo = ?
Cadmium	Cd = 111·7	Cd = Cd = 111·7
Indium	In = 113·4	In = 113·4
Tin	Sn = 117·35	Sn = ?
Antimony	Sb = 120	Sb = ?
Tellurium	Te = 126·3	Te = Te_2 = 252·6
Iodine	I = 126·53	I = I_2 = 253·06
Tantalum	Ta = 182	Ta = ?
Tungsten	W = 183·6	W = ?
Osmium	Os = 195	Os = ?
Mercury	Hg = 199·8	Hg = Hg = 199·8
Thallium	Tl = 203·7	Tl = ?
Lead	Pb = 206·39	Pb = ?
Bismuth	Bi = 207·5	Bi = ?
Uranium	U = 239·8	U = ?

[1] Above 800°. [2] At 500°. [3] Below 600°. Above this temperature molecules of Cl occur which = 35·37, and Br = 79·76; I = 126·53. At 1,200° these form half the weight or two-thirds the number of the molecules.

The preceding table contains the atomic and molecular weights of the elements which have up to the present time been determined by means of Avogadro's hypothesis. The atomic weights are placed after the initials of the names of the elements in Roman capitals, and the molecular weights after the corresponding Gothic capitals. The last column of the table shows the relation between the two values. The elements are arranged in the order of their atomic weights.

The table contains all the non-metals which are at present known. Nearly all the brittle or semi-metals are included in it, but only a very small number of the malleable ones, whilst all the lighter metals and many of the heavy metals are absent.

If the slight corrections which recent investigations have made in the stochiometric values are not taken into account, the atomic weights in the second column are identical with those which Berzelius represented by plain symbols,[1] with the exception of boron, silicon, vanadium, zirconium, niobium, and tantalum. Berzelius, however, generally took oxygen, and not hydrogen, as the standard for atomic weights.[2] But the atomic weights of about half the elements differ from Gmelin's so-called equivalent weights, which were for a considerable time the only values used. They are at present to be found in Leopold Gmelin's *Treatise on Chemistry*,[3] and in many other works, but have quite disappeared from recent text-books.

The return from Gmelin's atomic weights to those of Berzelius was not by any means accomplished so smoothly as could have been desired. The process of transition pursued a confused and devious course. As Gerhardt was guided solely by Avogadro's law and the chemical equivalents in his proposed reform of the system of organic chemistry, he was compelled, in the case of the non-metals and the semi-metals,

[1] The relation between the views of Berzelius and those now in vogue is discussed by Blomstrand, *Chemie der Jetztzeit*, &c. Heidelberg, 1869.

[2] The tables of atomic weights of 1826 (Berzelius, *Jahresber.* No. vii. 73) contain the values now in use for the atomic weights compared with hydrogen as unity, *e.g.* O = 16, S = 32·2, &c.

[3] L. Gmelin, *Handbuch der Chemie*, 5. Aufl. i. 46.

both of which form volatile compounds, to reintroduce those atomic weights which Berzelius had represented by non-barred symbols. In the case of the metals he did not proceed from a safe basis, and frequently fell into great errors. Like Gmelin, he selected hydrogen as the standard of atomic weight, but he differed from him by taking the simple atom H as the standard, and not the double atom $\ddot{H}$ of Berzelius, corresponding to the electrolytic equivalent of hydrogen. Consequently he ought to have represented the atomic weights of the metals by numbers twice as large as those which Gmelin and Berzelius had employed. But instead of so doing he retained Gmelin's numbers, and consequently halved the atomic weights without changing their symbols. But Gmelin had previously used the non-barred symbols of Berzelius to represent quantities of many of the semi- and non-metals which, when compared with the atomic weight of oxygen, were double the atomic weights used by Berzelius, and now Gerhardt employed the same symbols to represent quantities of the metals which were only equal to half the atomic weight accepted by Gmelin and Berzelius. Hence almost every atomic symbol has had two or often more distinct meanings assigned to it by different authors. To avoid this state of confusion Williamson [1] proposed to bar the symbols of all those atomic weights which bore double the value assigned to them by Gmelin. This was not a very happy suggestion, as the barred symbols of Berzelius had already been used by him to represent two atoms—the so-called double atom—and not one single atom. The barred symbols remained in use for some time in order to avoid confusion. They have now become superfluous, since, with a few exceptions which are universally acknowledged as necessary, the atomic weights of Berzelius have been reintroduced, so that there is no reason for any misunderstanding.

§ 26. It is shown in the table (p. 44) that Avogadro's hypothesis leads to the conclusion that the molecules of most of the so-called simple bodies are compounds of several atoms. This apparently surprising result is in complete accord with the properties and the behaviour of these bodies. Unless we

[1] *Ann. Chem. Pharm.* 1854, xci. 211.

assume that the elements in the so-called free state consist of atoms combined together to form groups, and not of isolated atoms, many of the properties of the elements which now admit of a very simple explanation would appear quite enigmatic. This is, indeed, the sole hypothesis which is capable of explaining satisfactorily the remarkable phenomena of the *status nascendi*.

It would be very difficult, unless this atomic grouping is assumed, to conceive why elements which only exhibit weak affinities in the so-called free state should enter into combination much more readily in the nascent state. But it is at once clear, if we consider, that in the free state the atoms are combined with each other to form regular groups or molecules; but that in the nascent state the individual atoms are isolated. In the first case, before an atom can form a new compound, it must overcome the force by which it is held in combination with the other atoms. But in the *status nascendi* there is no resistance to overcome and consequently the atoms will enter into combination much more readily. It is well known that oxygen and hydrogen in the free state do not combine when they are brought together at the ordinary temperature, but do so at a higher temperature, *i.e.* if the coherence of the molecules OO and HH is destroyed by raising the temperature. But at the moment when they are liberated and are in *status nascendi*, *i.e.* before their atoms have united together to form molecules, the combination of O with H_2 to form water takes place even at the ordinary temperature. Free carbon and free nitrogen belong to the class of the most inactive bodies known, since they not only unite with very few other substances but only enter into combination with these at very high temperatures. But they readily enter into new combinations when they are set free from any of their compounds. For example, it is with great difficulty that either of these elements combines directly with hydrogen, the combination, however, takes place readily when nascent hydrogen acts on their compounds with oxygen. Ammonia, NH_3, is easily formed in this way from nitric acid and from other oxygen compounds of nitrogen, though it is very difficult to obtain it from NN and HH, obviously because

the force which unites N with N and H with H must first be overcome.

A large number of so-called organic compounds are formed in the green leaves of plants, under the influence of light, by the carbon and hydrogen entirely or partially losing the oxygen with which they are combined, and satisfying the forces of affinity set free by union with each other.

These and numerous other cases would remain unexplained if it were not for this result of Avogadro's theory, which offers such a simple explanation of the facts.

§ 27. There still remains the possibility of assuming that the smallest quantities of the elements contained in the molecular weights of their compounds are not simple atoms but always groups of several atoms.

This idea is, however, directly opposed to the following very important observation. By determining the rate of the propagation of sound in the vapour of mercury, Kundt and Warburg[1] showed that the molecules of this vapour do not possess any internal movement, and do not, therefore, consist of several parts moving towards each other. Hence it is at least highly probable, although not positively proved, that the molecular weight is, as previously stated, equal to the atomic weight itself and not to one of its multiples. Judging by analogy, the atomic weights determined by Avogadro's method represent the correct values and not multiples of the true atomic weights.

§ 28. The preceding paragraphs contain the most valuable and the most important results which theoretical chemistry has derived from Avogadro's hypothesis. But in certain cases this hypothesis is capable of leading, and, indeed, has led, to considerable errors.

It has already been pointed out in § 17 that Avogadro's assumption that equal volumes of different gases and vapour at the same temperature and pressure contain the same number of particles cannot be strictly correct, since the volume occupied by different gases and vapours is not influenced to the same extent by changes of temperature or pressure. If equal volumes of oxygen and hydrogen under the pressure of

[1] *Ber. d. deut. chem. Ges.* 1875, 945; *Pogg. Ann.* 1879, clvii. 353.

one atmosphere contain the same number of particles, then under two atmospheres' pressure a volume of oxygen will contain more particles than a volume of hydrogen, for Regnault [1] has shown that one and the same increase of pressure produces a greater compression with oxygen than hydrogen. With the former the volume decreases in a slightly greater proportion than the pressure increases, whilst with the latter the decrease of volume is smaller than the increase of pressure. These deviations, which appear to depend on the dimensions of the particles and on the molecular forces acting between them, are in the case of most gases so small that they do not interfere with the determination of atomic and molecular weights by means of Avogadro's hypothesis. But the fact that Avogadro's law is only a very close approximation to the truth must not be lost sight of. The number of particles contained in equal volumes of different gases can, as a rule, be only approximately equal and is seldom absolutely equal. Besides these small deviations, others occur which either render the use of Avogadro's law impossible or permit of its use only under certain limits.

In the case of permanent gases and of vapours at temperatures far removed from their point of condensation, the deviations from Boyle's and Gay-Lussac's laws are so small that they may be neglected in the molecular weight determinations, but when the increase of pressure or diminution of temperature causes the vapours to approach their point of condensation, these deviations are considerably increased in the case of all substances which have hitherto been examined. The density increases much more rapidly than the relative fall of temperature or increase of pressure. But since the temperatures and pressures at which condensation takes place vary considerably for different bodies, it follows that the density of a vapour which is near its point of condensation cannot bear the same relation to the density of a permanent gas or to another gas which, at the same temperature and pressure, is more distant from its point of condensation, as would be the case if both vapours were considerably remote

[1] *Relation des Expériences*, &c. 1847, i. 6me mémoire, 329. This subject has been recently investigated by Amagat.

from their point of condensation, and consequently obeyed the general laws for the expansion of gases.

For example, Cahours[1] found that under the pressure of one atmosphere and at a temperature of 250° C., the density of acetic acid is 2·08 compared with air under similar conditions. This density corresponds to the molecular weight $C_2H_4O_2 = 59·86$.

Under the same pressure but at lower temperatures the density of the acid compared with the air at the same temperature increases with the diminution of temperature.[2] Thus Cahours found the density to be 3·20 at 125° C. A similar result is obtained if the observations are made under diminished pressure, but in this case a much greater diminution of temperature is required to produce the same increase in the density. The relative density increases with a constant temperature and an increasing pressure.[3]

The relative density of the vapour of acetic acid compared with air under similar conditions of temperature and pressure increases with an increased pressure as well as with a diminished temperature, or, in other words, the absolute density increases in each case more rapidly than that of air or of any other gas which follows the general laws of expansion. The question now remains whether Avogadro's hypothesis can be used in these cases. Since the density of the vapour gradually increases from 2·08, corresponding to the molecular weight $C_2H_4O_2$ to greater values, it is clear that the molecular weights calculated by Avogadro's rule from each of the observed densities will not correspond to a stochiometric quantity. The next higher value by which the composition of acetic acid, as found by analysis, can be represented is $C_3H_6O_3 = 89·8$, corresponding to the density $\frac{89·8}{28·87} = 3·11$. The next value is $C_4H_8O_4 = 119·7$, corresponding to the density $\frac{119·7}{28·87} = 4·15$. The molecular weights calculated by Avoga-

[1] Cahours, *Compt. Rend.* xix. 771; *Lieb. Ann.* lvi. 176.

[2] See the summary of observations of Bineau, Cahours, and Horstmann in Horstmann's article in the *Annalen*, 1868, vi. Suppl., 53.

[3] Alex. Naumann, *Lieb. Ann.*, 1870, clv. 325.

dro's law from the observed values of the relative density lying between 2·08 and 3·11 and between 3·11 and 4·15 cannot be represented by an empirical formula composed of whole atoms.

§ 29. This peculiar behaviour admits of two different explanations, both of which have, indeed, been offered by different authors. Horstmann[1] assumes that the vapour of acetic acid (and of all bodies behaving in a like manner) only contains the same number of particles as an equal volume of air under similar conditions when at high temperatures it exhibits the normal density 2·08, but that at lower temperatures it contains a larger number of particles.

On the other hand, Playfair and Wanklyn[2] assume that the vapour obeys Avogadro's law and contains the same number of particles as other vapours and gases; but a certain number of these particles have a larger molecular weight than the rest. Finally, it may be assumed that both the above causes act simultaneously.

But, according to the generally received theory of molecular impacts, the pressure of a gas or vapour is due to the collision of the particles moving at a high velocity. The first explanation, therefore, assumes that the velocity of the particles in a vapour, like that of acetic acid, possessing abnormally large density, is not proportional to the square root of the absolute temperature, but is influenced to a greater extent. Whilst, according to theory, equality of temperature, for all normal gases and vapours, consists in the equality of the mean kinetic energy of their particles, abnormal vapours would possess the same temperature as the normal gases and vapours (*i.e.* neither lose nor acquire heat when brought in contact with them), when the particles, instead of possessing the same kinetic energy, exhibited a proportionally smaller kinetic energy. But the relation between the mean kinetic energy of a particle of acetic acid and that of a particle of air at a fixed temperature would vary with the volume occupied

[1] A. Horstmann, *loc. cit.* p. 55.

[2] Playfair and Wanklyn, *Edin. Trans.* xxii. part iii. 441; *Lieb. Ann.* 1862, cxxii. 247. Consult also the articles by A. Horstmann and Alex. Naumann, which have been previously mentioned.

by the vapour of the acetic acid.[1] This explanation consequently meets with considerable difficulties, although it cannot be distinctly proved to be incorrect, in the present state of our knowledge of the conditions of equality of temperature.

The other hypothesis is more probable, viz., that the increased value of the abnormal densities is due to the fact that in the passage to the gaseous state the liquids are not at once directly split up into the smallest possible molecules, but larger aggregations of molecules remain together. A similar occurrence appears to take place (see Section VIII.) in the solution of solid bodies in liquids. Since the progressive velocity of the particles is, according to theory, regarded as inversely proportional to the square root of the molecular weight, the larger molecular aggregations must possess a smaller velocity corresponding to their greater mass, in order that their kinetic energy may be equal to that of the smaller particles. This explains why such a vapour (in spite of the larger mass contained in the volume) does not exert any greater pressure than would be the case if it were entirely composed of the smallest possible particles.

This hypothesis easily explains why the relative density (compared with air at the same temperature) under a constant temperature varies with the pressure, or, to use a different expression, changes with the absolute density. When the vapour is confined in a small space and the particles are crowded together, collisions between the particles must take place more frequently than when more space is allowed for their movement. But opportunity is offered for the formation of larger molecular aggregations each time the isolated smallest particles come into collision with each other. If the liquid is converted into vapour at a low pressure, it forms a certain quantity of smaller and larger molecules and aggregations of molecules. For a constant temperature, therefore, the

[1] Naumann's determinations of the vapour density of acetic acid at 100°, compared with air under the same pressure and temperature, give 3·4, when a litre of the vapour contains 1·68 gram of acetic acid, and only 2·6 when a litre contains 0·25 gram of the vapour. If the above assumption is correct, the kinetic energy of a single particle would be increased by rarefying the vapour in the proportion of 2·6 : 3·4, which is nearly equal to 3 : 4.

number of the larger aggregations will increase as the vapour is compressed into a smaller volume. That it is not completely condensed to larger aggregations or to the liquid state is due to the rapid movement of the particles at the existing temperature; a part of the larger aggregations which are formed being continually decomposed. A state of equilibrium ensues when the formation and decomposition of the molecular aggregations are equal. It is obvious that when the vapour expands to a larger volume the collision between the particles and the formation of larger aggregations will become less frequent, whilst the decomposition of the groups gains ground, consequently the larger particles will decrease and the smaller particles will increase in number.

At present the value to be ascribed to the larger aggregations can hardly be determined. It has been suggested that these larger groups are composed of two of the smallest particles, so that the vapour would consist of molecules of $C_2H_4O_2$ and $C_4H_8O_4$.[1] Horstmann[2] has already pointed out that the existence of the acid potassium salt $KC_4H_7O_4$ appears to favour this hypothesis. This idea, however, is based on very feeble grounds. It is quite as probable that the larger aggregations are built up very irregularly from simple and complicated particles. This question cannot at present be decided. It can only be said with certainty that above a certain limit of temperature and pressure[3] the molecular weight of acetic acid is represented by $C_2H_4O_2$, whilst below this limit molecules of the above composition are mixed with larger particles, the value of which is at present unknown.

§ 30. It is only above a certain limit of temperature, which varies with the pressure, that Avogadro's law for determining the molecular weight yields for acetic acid and most other vapours a value corresponding to the stochiometric quantity. Below this limit larger values are obtained which cannot be

[1] Playfair and Wanklyn, *loc. cit.*

[2] *Loc. cit.* 55.

[3] Cahours fixes this limit at 250° for a pressure of one atmosphere. Under a pressure of 100 mm. the limit lies at about 200°, according to Naumann's experiments, which are not perfectly conclusive.

To obtain whole atomic numbers in the formulæ of ammonium carbamate and chloride, the atomic weight of nitrogen would have to be reduced to one-sixth the present value, or $\frac{14{\cdot}01}{6} = 2{\cdot}335$. And in almost all other compounds of this element, even in the most simple, it would be necessary to assume the existence of at least six atoms.

The vapour density of cinnabar, determined by Mitscherlich (5·51 and 5·68) [1] and by V. Meyer (5.39),[2] yields the corrected molecular weight $\frac{3}{2}$Hl = 154·5, containing $133{\cdot}2 = \frac{2}{3} \times 199{\cdot}8$ parts by weight of mercury, and $21{\cdot}3 = \frac{2}{3} \times 31{\cdot}98$ parts of sulphur. It would therefore be necessary to reduce the atomic weights of these elements to one-third of their present values.

In order to avoid these unusual and inconvenient conclusions, certain chemists, H. Sainte-Claire Deville in particular, have disputed the accuracy of Avogadro's hypothesis, and have again supported the notion, which was formerly current, viz. that many substances, such as ammonium chloride and ammonium carbamate, contained respectively in the gaseous state only half or a third as many molecules in a given volume as is contained in most other gases under similar conditions. These views, which are obviously incorrect, have not of late met with any support.

§ 31. Mitscherlich [3] had previously observed that antimony pentachloride, $SbCl_5$, which is analogous in composition to phosphorus pentachloride, decomposes into $SbCl_3$ and Cl_2 when volatilised.

Gladstone [4] pointed out the decomposition of phosphorus bromide, PBr_5, into PBr_3 and Br_2. The products of decomposition being in each case separated by their difference in volatility.

When $SbCl_5$ or PBr_5 is heated in an imperfectly closed vessel, and a current of an indifferent gas allowed to pass through the substance, the easily volatile Cl_2 and Br_2 are carried off, and the less volatile compounds, $SbCl_3$ and PBr_3,

[1] *Pogg. Ann.* 1833, xxix. (cv.), 225.
[2] *Ber. d. deut. chem. Ges.* 1879, 1118.
[3] *Pogg. Ann.* 1833, xxix. (cv.), 227.
[4] *Phil. Mag.* [3], 1849, xxxv. 345.

remain behind or are condensed in the cooler portions of the vessel. From these and similar observations, S. Cannizzaro,[1] H. Kopp,[2] and A. Kekulé[3] arrived simultaneously, though independently, at the conclusion that a similar decomposition takes place in the volatilisation of any other compounds of N, P, As, Sb, &c., which contained more than three atoms of chlorine, bromine, iodine, or hydrogen, *e.g.* phosphorus pentachloride, ammonium chloride.[4]

This hypothesis offers a very simple explanation of the apparently abnormal behaviour of these substances. They do not in reality form an exception to Avogadro's rule; on the other hand, they contain in the gaseous state just as many molecules in a given space as any other gases. But these molecules are not homogeneous; in the case of the chlorides and bromides, for example, half the molecules have the composition $SbCl_3$ or PBr_3, and the others Cl_2 or Br_2, &c.

The density of the mixture is therefore the arithmetical mean of the densities of a mixture of equal volumes of the two substances.

Similarly, the density of the gas produced by volatilising ammonium chloride, viz., 0·89, is the mean of the densities of hydrochloric acid (1·25) and ammonia (0·59), and the apparent molecular weight, $26·69 = N\frac{1}{2}H_2Cl\frac{1}{2}$, calculated from the density by Avogadro's law, is nothing more than the arithmetical mean of the molecular weights of the two constituents—

$$N\tfrac{1}{2}H_2Cl\tfrac{1}{2} = \frac{NH_3 + HCl}{2} = \frac{17·01 + 36·37}{2} = 26·69.$$

If ammonium carbamate decomposes into two volumes of ammonia and one of carbon dioxide, according to the equation $N_2H_6CO_2 = NH_3 + NH_3 + CO_2$, it will form a gas having a density equal to one-third of the sum of the densities of its constituents (0·59 for ammonia, and 1·53 for carbon dioxide).

[1] 'Nota sulle Condensazioni di Vapore,' appended to *Sunto di un Corso di Filosofia Chimica*, Pisa, 1856, xv. *Nuovo Cimento*, vi. 1857, p. 428.

[2] *Lieb. Ann.* 1858, cv. 390.

[3] *Ibid.* cvi. 143. See also Kekulé's *Lehrbuch*, i. 443.

[4] See Kopp, *Jahresbericht*, 1859, 27.

This is really the case, since the density 0·89 observed by H. Rose is equal to

$$\frac{0{\cdot}59+0{\cdot}59+1{\cdot}53}{3}=0{\cdot}90,$$

and corresponds to the apparent molecular weight

$$N\tfrac{2}{3}H_2C\tfrac{1}{3}O\tfrac{2}{3}=\frac{2NH_3+CO_2}{3}=\frac{2\,.\,17{\cdot}01+43{\cdot}89}{3}=25{\cdot}97.$$

These purely hypothetical views soon received experimental confirmation in the case of several different substances. Pebal[1] first proved the decomposition of ammonium chloride by separating it into ammonia and hydrochloric acid by means of diffusion in an atmosphere of hydrogen.

By a similar process Wanklyn and Robinson[2] proved the decomposition of phosphorus pentachloride into phosphorus trichloride and chlorine.

H. Sainte-Claire Deville[3] brought together hydrochloric acid and ammonia at 350°, a temperature at which ammonium chloride is volatilised, and is therefore decomposed according to the above hypothesis. He believed that the temperature rose to 394·5°, and concluded from this rise in temperature that the two substances had entered into chemical combination, and consequently the vapour of ammonium chloride is a chemical compound, and not a mixture of ammonia and hydrochloric acid.

But K. Than[4] repeated the same experiment, and by using a better method showed that no appreciable evolution of heat occurred, as would have been the case if chemical combination had taken place.

This experiment has also been confirmed by the more recent observation of Marignac[5] that the amount of heat required to volatilise ammonium chloride is equal to the heat liberated in its formation from hydrochloric acid and ammonia. Hence, according to the principles of the mechanical theory of heat,

[1] *Lieb. Ann.* 1862, cxxiii. 199.

[2] *Lond. Roy. Soc. Proc.* xii. 507. Will, *Jahresbericht der Chem.* 1863, 38.

[3] *Compt. Rend.* lvi. 729; *Lieb. Ann.* 1863, cxxvii. 108. See also Kopp, *ibid.* p. 280.

[4] *Lieb. Ann.* 1864, cxxxi. 129.

[5] *Compt. Rend.* lxviii. 877; Strecker's *Jahresbericht*, 1868, 71.

ammonium chloride must have been decomposed into its original constituents.

A few years later, H. Sainte-Claire Deville,[1] who had denied the decomposition of all these compounds, gave a proof of the decomposition of phosphorus pentachloride by showing that the vapour of this compound possesses the colour of chlorine diluted with a colourless gas, and that the intensity of the colour increases with the temperature.

It is now universally regarded as beyond doubt that all these compounds are really decomposed. There is therefore no necessity to reject Avogadro's hypothesis or to reduce in the manner indicated the atomic weights deduced by its aid.

§ 32. A number of cases have been observed in which the vapour densities of compounds have been found to be greater than the mean density of the products of decomposition, supposing the decomposition to have taken place entirely in the manner described above. Deville and Troost[2] obtained results differing from those of Bineau. They found that the density of the vapour of ammonium chloride is 1·01 at 350° C. and 1·00 at 940° (the boiling point of zinc), compared with air under similar conditions of temperature and pressure, whereas a mixture of equal volumes of hydrochloric acid and ammonia has the density 0·92, but a compound with the molecular weight, $NH_4Cl = 53{\cdot}38$, would have a density of 1·84.

Similar observations have been made by different investigators with other substances, and it has been placed beyond dispute that the deviations of the observed values from the calculated numbers are in many cases too large to arise from errors of observation. These deviations are exceptionally large in the case of phosphorus pentachloride, the density of which, compared with air, was found by Cahours[3] at temperatures above 300° to be 3·66, whilst the calculated density of a mixture of equal volumes of PCl_3 and Cl_2 is 3·61. Above 300° it is completely, or almost completely, split up into phosphorus trichloride and chlorine.

[1] *Compt. Rend.* 1866, lxii. 1157.

[2] *Ibid.* 1859, xlix. 239, and 1863, lvi. 891.

[3] *Ann. Chim. Phys.* [3] 1847, xx. 369; Liebig and Kopp, *Jahresbericht*, 1847–8, 364.

Below this temperature considerably larger values were found for the density. Cahours obtained the following results:

Temperature.	Density.	Temperature.	Density.
182° C.	5·08	288° C.	3.67
190°	4·99	289°	3·69
200°	4·85	300°	3·65
230°	4·30	327°	3·66
250°	3·99	336°	3·66
274°	3·84		

Later determinations made by Cahours [1] at 170° and 172° yielded still higher values than those obtained at 182°. These new results have, however, not been published.

Würtz [2] afterwards found that the vapour of phosphorus pentachloride mixed with air at low temperatures, and with PCl_3 at temperatures below 160° and 175°, possesses a much greater density than would be the case if it decomposed into chlorine and trichloride.

Experiments with mixtures of phosphorus tri- and pentachlorides show that such a mixture occupies in the state of vapour the same volume which would, under similar external conditions, be filled by the vapour of the pure trichloride containing the same amount of phosphorus. The quantities $n\,PCl_3 + m PCl_5$, and $(n+m)PCl_3$ form almost exactly the same volumes of vapour under similar conditions of pressure. In these experiments the values of n and m vary considerably, but m was never equal to more than half n. Whether the mixed vapours would exhibit the same phenomenon beyond these limits has not been ascertained.

These observations made by Würtz can only be explained on the assumption that the vapour from a mixture of the two chlorides forms only as many molecules as there are phosphorus atoms, and consequently it consists of PCl_3 and PCl_5, and not of PCl_3 and Cl_2.[3]

Hence it is very probable that the vapour of the penta-

[1] *Compt. Rend.* lxiii. 14; *Lieb. Ann.* 1867, cxli. 42.

[2] *Bull. Soc. Chim.*, April 2, 1869; *Ber. deut. chem. Ges.* 1869, 162, and 1870, 572; *Compt. Rend.* 1873, lxxvi. 607.

[3] The correctness of the experiments by Würtz can be proved by mixing chlorine and the vapour of phosphorus trichloride at 160°–175°, when a considerable contraction will ensue.

chloride at temperatures between 175° and 300°, still contains molecules of the composition PCl_5, whilst a part of the pentachloride splits up into PCl_3 and Cl_2. This decomposition increases as the temperature approaches 300°, at which point all the particles of PCl_5 are decomposed.

This hypothesis agrees with the observations of Sainte-Claire Deville and Würtz that the denser the vapour the less it exhibits the colour of chlorine.

§ 33. The study of other compounds the density of which in the gaseous state is abnormal has yielded results, giving a clearer insight into the nature of the phenomena exhibited by the vapours of phosphorus pentachloride, &c.

This is especially true in the case of the compounds of amylene, C_5H_{10}, with HCl, HBr, and HI. Würtz discovered and investigated the interesting behaviour of these compounds. According to the investigations of Würtz, amylene hydrobromide,[1] $C_5H_{11}Br$, exhibits, under a pressure of one atmosphere and at a temperature between 150°–180°, the vapour density 5·2, compared with air under similar conditions of temperature and pressure, which corresponds to the molecular weight, $C_5H_{11}Br = 150·6$.[2] On raising the temperature the density decreases, first slowly, then rapidly, and finally slowly again, until it is only 2·6 at 360°.

The density of a mixture of equal volumes of C_5H_{10} and HBr is 2·6, and Würtz was able to prove the presence of these constituents in the vapour. Hence it is placed beyond doubt that the compound which volatilises at 180° with the molecular weight $C_5H_{11}Br$ is completely decomposed at 360° into C_5H_{10} and HBr, which unite together again at a lower temperature. H. Sainte-Claire Deville has assigned the special name of Dissociation to the class of phenomena where the rate of decomposition of a compound increases with a rise and diminishes with a fall of temperature.

These phenomena will be studied in detail in the section treating of chemical changes under the influence of heat.

§ 34. In the descriptions given hitherto of the methods now in use for determining the atomic weights an omission still

[1] The bromide of methyl isopropyl carbinol.

[2] Ad. Würtz, *Compt. Rend.* lx. 728; *Ann. Chem. Pharm.* 1865, cxxxv. 315.

exists. The rule that the smallest quantity of an element occurring in a molecule of the compound is to be regarded as an atom is obviously inadequate. It assumes that every element forms at least one compound capable of existing in the gaseous state, which is known to contain only one atom in the molecule, and is therefore of all possible compounds the one which contains the smallest quantity of this element in a given volume, or is, in other words, the compound in which the given element occurs in the highest state of dilution, or in the lowest state of condensation.

It is probable that we shall never be able to assert with absolute certainty that such a compound is known in the case of each element. The probability that just the compounds known in the gaseous state fulfil this condition is evidently small in all cases where only a very small number of the gaseous compounds of an element are known.[1]

The knowledge of the molecular weight, *i.e.* of the vapour density, is, strictly speaking, only sufficient to determine a maximum limit for the value of the atomic weight. Since an atom is regarded as that mass which cannot be further decomposed by chemical decomposition, the atom of an element cannot be larger than the amount of this element which is contained in the molecule of any one of its compounds. If, for instance, every known oxygen compound contains at least 15·96 unit weights of oxygen in the molecule, we conclude that the atom of oxygen cannot weigh more than 15·96 units. But it has not been proved that this quantity does not consist of two or more atoms firmly united together, in which case the atomic weight of oxygen might be regarded as equal to 7·98, or in round numbers 8. In reality for a considerable length of time this was the case.

In the theoretical natural sciences it seldom happens that a general result obtained by speculation, or a principle deduced from empirical material, acquires its full import so long as it is supported by results arrived at from one point of view. The value of such a theoretical conclusion is greatly enhanced when the same result is obtained by totally different methods.

This is true to the fullest extent of the atomic weights

[1] See § 24.

deduced from the densities of gases and vapours. The knowledge of the density does indeed permit of further deductions concerning the relative weight of the atoms than those arrived at in the previous pages. But the values of the atomic weights would not possess that degree of probability, bordering on certainty, had not Cannizzaro [1] clearly and convincingly shown that these values are confirmed by their intimate relation to another property of matter, viz., specific heat. An acquaintance with the specific heat of an element consequently forms a second valuable means of determining its atomic weight.

[1] *Sunto di un Corso di Filosofia Chimica.* Pisa, 1858. See also Kopp and Will, *Jahresbericht*, 1858, 11.

III.

THE DETERMINATION OF ATOMIC WEIGHTS FROM THE SPECIFIC HEAT OF MATTER IN THE SOLID STATE.

§ 35. As EARLY as the year 1819 Dulong and Petit [1] were led, by their careful measurements of the specific heats of thirteen chemical elements, to the interesting and important conclusion that the specific heats of these elements (referred to the unit of weight) are inversely proportional to their atomic weights. And consequently the specific heat is directly proportional to the number of atoms contained in the unit of weight. The relative specific heat of the atoms is obtained by multiplying the specific heat by the atomic weight; this product of the specific heat and atomic weight was found to be equal in the case of all the elements investigated. Based upon these facts these observers founded the general law, that 'the atoms of all elementary bodies possess the same specific heat.'

From the simplicity of this law proposed by Dulong and Petit, it might have been expected that it would have received immediate acknowledgment and acceptance at the hands of chemists. But such an immediate and unreserved acceptance was rendered impossible owing to the scepticism of chemists; and, as a matter of fact, such an action would have proved rash and precipitate.

The atomic weight of an element cannot be finally fixed by chemical analysis alone, the results always leave a choice between several numbers, which bear a simple relation to one another. Dulong and Petit therefore, in order to make their law applicable to all elements the specific heats of which they had determined, made certain changes in the atomic weights

[1] 'Recherches sur quelques points importans de la théorie de la chaleur,' *Ann. Chim. Phys.* x. pp. 395–413.

then in use. Thus in the case of the four elements, bismuth, platinum, silver, and cobalt, they substituted multiples or sub-multiples of the atomic weights then in use; and, further, the atomic weights of all metals in relation to that of sulphur were diminished to half the values assigned to them by Berzelius. These proposed changes in atomic weights called forth adverse criticisms. Berzelius,[1] the first authority in this province, justly demanded a further extension of these investigations; in the meanwhile he was of the opinion that a successful application of these ideas to compound bodies would form the basis of one of the most beautiful fields of chemical theory.

§ 36. Dulong and Petit did not succeed in satisfying this demand. F. Neumann[2] made the first successful advances in this direction, showing, in the year 1831, that equivalent quantities of compounds possessing analogous composition have the same specific heats. Further, this equality is not due to the similarity in crystalline form, frequently observed in compounds of analogous composition, since compounds, having the same composition but differing in their crystalline form (*e.g.* calc spar and arragonite), also possess the same specific heat. Neumann did not attempt to bring the law, which he had discovered for different groups of compounds, into direct relation with the law of Dulong and Petit. An attempt to do this was unsuccessfully made by Avogadro,[3] who shortly afterwards published a number of determinations of the specific heat of simple and compound bodies; these determinations were not, however, very trustworthy.[4]

The recognition of the connection between the specific heat of compounds and that of their constituents has taken place gradually, but not without receiving several erroneous interpretations. The development of this subject is especially due to the labours of R. Hermann, V. Regnault, De la Rive

[1] In his first *Jahresbericht*, German edition, p. 19, and in *Jahresbericht*, xxi. 6.

[2] 'Untersuchung über die specifische Wärme der Mineralien,' *Pogg. Ann.* xxiii. 1.

[3] *Memorie della Società italiana delle Scienze*, xx.; *Ann. Chim. Phys.* 1834 lv. 80 and lvii. 113.

[4] Regnault's criticism. *Ann. Chim. Phys.* 1840, lxxiii. 10.

and Marcet, H. Schröder, A. C. Woestyn, H. Kopp,[1] and H. F. Weber, and may still be regarded as incomplete.

§ 37. The further progress in the investigation of specific heat demonstrated very clearly, how justifiable was the caution with which Berzelius and his disciples accepted those changes in the atomic weights, based upon the determination of specific heats.

This caution was warranted by the experimental difficulties [2] in the determination, leading to uncertainty in the results, and was further increased by the doubtful purity of the substance used to determine the specific heats. On the other hand, with increased accuracy in the methods adopted, it was evident that the specific heat of a substance itself is not a constant but rather a very variable magnitude. Consequently the law of Dulong and Petit could only be accepted as an approximation, as stated by Avogadro in 1834,[3] and demonstrated to be so later on by Regnault.[4]

Observations show that, as a rule, the specific heat increases with increase of temperature; with the same substance, it is greater in the state of liquid than in the solid state, *e.g.* in the case of water and iodine the specific heat of the liquid is twice that of the solid. And in the case of metals the specific heat is lessened by compression. Further, allotropic forms of a substance have often totally distinct specific heats, *e.g.* under similar conditions diamond and graphite, the two allotropic forms of carbon, possess different specific heats.

All these conditions had first to be explained by an extensive and reliable series of observations, before theoretical chemistry could receive a lasting benefit from the discoveries of Dulong and Petit and Neumann. Regnault has done more than any other investigator to render these discoveries of service to the science. For, by means of the numerous

[1] An account of the share taken by these and other investigators in the development of this subject will be found in Kopp's paper, entitled 'Untersuchungen über die spec. Wärme,' *Ann. Chem. Pharm.* 1864, Suppl.-Bd. iii. 5.

[2] Dulong and Petit found the specific heat of metallic cobalt to be so great that it necessitated the reduction of the atomic weight to two-thirds of the value then accepted.

[3] *Op. cit.* lv. 80.

[4] *Op. cit.* lxxiii. 66.

observations of this author made since 1840,[1] the validity of the law of Dulong and Petit has been established for a large number of elements, and Neumann's law has been materially extended. The values obtained by Regnault have since this time formed the real basis of all chemical speculations on the relationship between specific heats and atomic weights.

The investigations of Regnault have shown beyond doubt that Dulong and Petit's law applies with close approximation in the case of the majority of some forty of the elements investigated. And for these elements those values may be regarded as the atomic weights, which, when multiplied by the specific heats, yield the same product in each case. This product represents the specific heat of the atom, and is usually styled the atomic heat. Taking the atomic weight of hydrogen as unit, and the specific heat of water as one, then the values obtained for the above product lie between 5 and 7; for the majority of the elements it is a little greater than 6, viz. 6·4. If the atomic weights are expressed in terms of that of oxygen, as was done by Berzelius, the atomic weight of oxygen being 100, then the values obtained for the above product approximate to 40. In such cases, however, it is always supposed that the specific heats have been determined under similar conditions, viz. that the substances are solid and the temperature of observation is considerably lower than the melting point of the substance. The deviations are always greater in cases where these conditions cannot be sufficiently satisfied.

Regnault also pointed out that in the case of certain elements the atomic weight deduced from the determination of the specific heat could not be accepted as the true atomic weight. The specific heats of these elements have been redetermined by H. F. Weber,[2] with the aid of Bunsen's ice calorimeter, and the influence of temperature upon them sub-

[1] *Ann. Chim. Phys.* 1840, lxxiii. 5; [3] 1840, i. 129; 1843, ix. 322, and later publications in the *Compt. Rend.* and *Ann. Chim. Phys.*

[2] *Die specifischen Wärmen der Elemente Kohlenstoff, Bor und Silicium.* 1. Abhandlung, 'Die Abhängigkeit der spec. Wärme der isolirten Elemente Kohlenstoff, Bor und Silicium von der Temperatur.' Von Dr. H. F. Weber. Stuttgart, Mezler, 1874. *Pogg. Ann.* 1875, cliv. 367. For a short notice of part of this work, see *Berichte deut. chem. Ges.* 1872, v. 303.

mitted to a very thorough examination. These investigations show that the law of Dulong and Petit is applicable to these elements, but only within certain limits of temperature, above or below which the law no longer holds true.

§ 38. Prior to the determinations of Weber, the specific heats of the elements boron, carbon, and silicon had been determined only at temperatures lying between the freezing and boiling points of water. Accepting the atomic weight of these elements as deduced by the aid of Avogadro's law, then the specific heats so determined were much smaller than those required by the law of Dulong and Petit.

Not only were different values obtained for the specific heats of the allotropic modifications of one and the same element, but different observers attributed very different values to the same modification of the same element. Weber concluded, from an exact comparison of the determinations hitherto made, that these differences might possibly arise from the variation of the specific heats of these elements under the influence of temperature. The results of an extensive series of experiments confirmed this view; in these experiments the specific heat of carbon was determined for temperatures varying from $-80°$ to $1060°$ C.; that of boron and of silicon for temperatures between $-80°$ and $+260°$ C. Further it was shown that above a certain fixed temperature the specific heat becomes constant, and is then subservient to the law of Dulong and Petit. In the case of silicon this limit was found to be $200°$ C., and for the different modifications of carbon at a red heat, or about $600°$ C. Although in the case of boron this limit has not been directly determined, yet the observations made with this substance exhibit such a similarity in behaviour to that of carbon that the limit may, with a probability approaching to a certainty, be accepted as lying between $500°$ and $600°$ C. At the same time Weber confirmed the observation of former experimenters, viz. that graphite below a red heat has a much higher specific heat than diamond, but found that at a red heat this difference became so small that it could no longer be measured with accuracy. Contrary to former observation, it was found that in regard to specific heat no difference is exhibited by graphite,

compact coal (from Wunsiedel), and porous charcoal; and therefore carbon, as regards its thermal properties, exists in two modifications only, viz. the transparent and opaque varieties. Further, that at a red heat, where their optical differences cease to exist, these allotropic modifications behave as one and the same substance. Boron and silicon apparently exhibit similar properties. According to Nilson and Pettersson [1] the specific heat of beryllium also varies to a marked degree with the temperature. It increases with a rise in temperature more rapidly than the specific heat of silicon, but less than that of carbon and boron.

The following table contains the results obtained by Weber and Nilson and Pettersson. The description of the element is given in column I.; column IIa. shows the specific heats determined at the temperature t, given in column III., that of water at 0° being the unit. These numbers represent that fraction of a unit of heat which is required to raise the temperature of the unit weight of the substance from $t°$ to $(t+1)°$ C. Since these numbers could not be directly deduced from experiment, they were calculated by interpolation from the amounts of heat taken up or given out in heating or cooling through a given interval of temperature. Hampe [2] has shown that boron crystallised in octahedra and regarded as pure is a compound containing 13 % Al, 3·78 % C, and 83·22 % B, and having the formula $C_2Al_3B_{48}$. Since Weber used this variety his results have been recalculated on the assumption (1) that the specific heat of aluminium is that obtained by V. Regnault and H. Kopp, viz. at 0° = 0·20, and at 23·3° = 0·23, and that between these temperatures the changes are proportional to the temperature; (2) that carbon is contained in these crystals in the form of diamond. The results of these calculations are given in the column IIb. The column IV. contains the numbers representing the increase in the specific heat for each degree for the interval of temperature in question. Column V. contains the atomic weight as determined by Avogadro's law, and in VI. are the products of the specific heat into the atomic weights.

[1] *Berichte deut. chem. Ges.*, xiii. 1451, 1784.
[2] *Lieb. Ann.* 1876, clxxxiii. 98.

SPECIFIC HEATS OF BORON, CARBON, SILICON, AND BERYLLIUM.

I.	IIa. c'	IIb. c	III. t	IV. Δc	V. A	VI. $A.c$
Boron in octahedral crystals	0·1915	0·196	−39·6°	—	10·9	2·14
				0·000800		
„ „	0·2382	0·249	+26·6		„	2·71
				0·000788		
„ „	0·2737	0·289	+76·7		„	3·14
				0·000757		
„ „	0·3069	0·326	+125·8		„	3·55
				0·000675		
„ „	0·3378	0·360	+177·2		„	3·92
				0·000543		
„ „	0·3663	0·391	+233·2	—	„	4·26
Carbon: (1) Diamond	—	0·0635	−50·5		11·97	0·76
				0·000802		
„ „	—	0·0955	−10·6		„	1·15
				0·000812		
„ „	—	0·1128	+ 10·7		„	1·35
				0·000837		
„ „	—	0·1318	+ 33·4		„	1·58
				0·000859		
„ „	—	0·1532	+ 58·3		„	1·84
				0·000856		
„ „	—	0·1765	+ 85·5		„	2·12
				0·000831		
„ „	—	0·2218	+140·0		„	2·66
				0·000779		
„ „	—	0·2733	+206·1		„	3·28
				0·000716		
„ „		0·3026	+247·0		„	3·63
				—		
„ „		0·4408	+606·7		„	5·29
				—		
„ „	—	0·4489	+806·5		„	5·39
				—		
„ „	—	0·4589	+985·0		„	5·51
				—		
„ (2) Graphite	—	0·1138	− 50·3		„	1·37
				0·000749		
„ „	—	0·1437	− 10·7		„	1·73
				0·000777		
„ „	—	0·1604	+ 10·8		„	1·93
				0·000764		
„ „	—	0·1990	+ 61·3		„	2·39
				0·000715		
„ „	—	0·2542	+138·5		„	3·05
				0·000672		
„ „	—	0·2966	+201·6		„	3·56
				0·000596		
„ „	—	0·3250	+249·3		„	3·88
				—		
„ „	—	0·4454	+641·9		„	5·35
				—		
„ „	—	0·4539	+822·0		„	5·45
				—		

SPECIFIC HEATS OF BORON, CARBON, SILICON, AND BERYLLIUM—*continued.*

I.	IIb. *c*	III. *t*	IV. Δ *c*	V. *A*	VI. *A.c*
Carbon : (2) Graphite .	0·4670	+977·9°		11·97	5·50
			—		
Silicon, crystalline .	0·1360	− 39·8		28	3·81
			0·000550		
,, ,, .	0·1697	+ 21·6		,,	4·75
			0·000382		
,, ,, .	0·1833	+ 57·1		,,	5·13
			0·000235		
,, ,, .	0·1901	+ 86·0		,,	5·32
			0·000148		
,, ,, .	0·1964	+128·7		,,	5·50
			0·000085		
,, ,, .	0·2011	+184·3		,,	5·63
			0·000038		
,, ,, .	0·2029	+232·4		,,	5·68
			—		
Beryllium[1] . . .	0·3973	+ 23·0		9·1	3·62
			0·00101		
,, . . .	0·4481	+ 73·0		,,	4·08
			0·00085		
,, . . .	0·5193	+157·0		,,	4·73
			0·00063		
,, . . .	0·5819	+257·0		,,	5·29

Although the determinations of the specific heats of these three elements made previous to Weber's experiments have but little value for the determination of the atomic weight, yet for the sake of completeness they are given in the following table. No mention is made of the cases where a porous form of carbon has been used, since the results are vitiated by the heat produced in the absorption of water by the carbon (Weber, *loc. cit.*) The arrangement of the following table is similar to that of the former, save that in column IV. the names of the observers are given with the following abbreviations :—Rg. for V. Regnault,[2] Kp. for Kopp,[3] B.W. for Bettendorf and Wüllner,[4] M.D. for Mixter and Dana.[5] The

[1] The values for the real specific heats were calculated by L. Meyer from the apparent specific heat. *Ber. deut. chem. Ges.* 1880, xiii. 1784.

[2] *Ann. Chim. Phys.* [3] 1841, i. 202–205 ; 1861, lxiii. 24–38 ; [4] 1866, vii. 450–462.

[3] *Lieb. Ann.*, 1864 and 1865 ; Suppl.-Bd. iii. 63–73.

[4] *Pogg. Ann.* 1868, cxxxiii. With regard to the calculations from these observations, *vide* Weber (*loc. cit.*)

[5] *Lieb. Ann.* 1873, clxix. 388.

temperatures given in column III. are calculated on the assumption that the specific heat within the limits of temperature of observation varies directly with the temperature; Weber, however, has shown that this assumption is only approximately true.

I.	II. c	III. t	IV. Observer	V. A	IV. $A.c$
Boron, amorphous .	0·254	+ 36°	Kp. 1864	B = 10·9	2·8
„ crystalline .	0·230	+ 36	„	„	2·5
„ „ [1] .	0·252	+ 50	M.D. 1873	„	2·7
„ „ .	0·262	+ 54	Rg. 1861	„	2·9
„ „ .	0·225	+ 55	„	„	2·5
„ „ .	0·257	+ 57	„	„	2·8
„ graphitic .	0·235	+ 58	„	„	2·6
Carbon:					
(*a*) Diamond . .	0·143	+ 47	B.W. 1868	C = 11·97	1·7
„ . .	0·147	+ 54	Rg. 1841	„	1·8
(*b*) Artificial graphite	0·165	+ 36	Kp. 1864	„	2·0
„ „ .	0·186	+ 45	B.W. 1868	„	2·2
„ „ .	0·197	+ 55	Rg. 1841	„	2·4
(*c*) Natural graphite .	0·174	+ 36	Kp. 1864	„	2·1
„ „ .	0·188	+ 46	B.W. 1868	„	2·3
„ „ .	0·198	+ 57	Rg. 1866	„	2·4
Silicon, fused . .	0·138	+ 35	Kp. 1864	Si = 28	3·9
„ „ .	0·166	+ 60	Rg. 1861	„	4·6
„ crystalline .	0·165	+ 35	Kp. 1864	„	4·6
„ „ [2] .	0·171	+ 50	M.D. 1873	„	4·8
„ „ .	0·173	+ 60	Rg. 1861	„	4·8

§ 39. The influence of temperature on the specific heats of these three solid elementary bodies is much greater than in the case of the other elements the specific heats of which have been determined. In all cases, however, an increase in the specific heat with rise in temperature has been observed, but this increase is similar to that exhibited by carbon above a red heat, and by silicon at temperatures from 200° upwards. As a rule, a greater increase in the specific heat is observed when the temperature of observation is near the melting point of the substance, except in the case of those elements which soften before melting, when the increase in the specific heat is noticed many degrees below the melting point. The specific

[1] This sample was analysed, and the specific heats of the impurities deducted.

[2] This sample of silicon was analysed, and allowances made for the specific heats of the impurities.

heats determined at temperatures sufficiently removed from the melting point, obey the laws of Dulong and Petit; *i.e.* for each element a number may be obtained representing the thermal atomic weight, which when multiplied into the specific heat gives the atomic heat; a value which is approximately the same for all elements.

The following table gives a summary of the elements the specific heats of which in the solid state have been determined with anything like accuracy.[1] The names of the elements are given in column I., in II. under *c* are given the specific heats, that of water being taken as the unit, and in III. under *t* are given the temperatures of observation;[2] the column IV. gives the names of observers with the following abbreviations :—Rg. for Regnault,[3] Kp. for Kopp,[4] N. for Neumann,[5] B.W. for Bettendorf and Wüllner,[6] Bn. for Bunsen,[7] Wb. for H. F. Weber,[8] M.D. for Mixter and Dana,[9] H. for Hildebrand,[10] Ni. for Nilson, N.P. for Nilson and Pettersson,[11] Bt. for Berthelot,[12] Z. for Zimmermann;[13] column V. under *A* contains those values which must be accepted as atomic weights (H = 1) in order that the products obtained by multiplying them into the specific heats may be approximately 6·4; column VI. under *A.c* contains the atomic heats, *i.e.* the product of the atomic weight into the specific heat.

[1] A very complete summary is given of these determinations in No. 276 of the *Smithsonian Miscellaneous Collection*, 'The Constants of Nature,' pt. ii., compiled by F. W. Clarke, Washington, 1876.

[2] These temperatures are the arithmetical mean of the extreme temperatures at which the specific heats were determined. For B, C, Si, Be, *vide* § 38.

[3] *Ann. Chim. Phys.* [2] 1840, lxxiii. 5; [3] 1841, i. 129; 1843, ix. 322; 1849, xxvi. 261; 1853, xxxviii. 129; 1856, xlvi. 257; 1861, lxiii. 5; 1862, lxvii. 427.

[4] *Lieb. Ann.* 1863, cxxvi. 362; 1864 and 1865; Suppl.-Band, iii. 1 and 289.

[5] *Pogg. Ann.* 1865, cxxvi. 123.

[6] *Ibid.* 1868, cxxxiii. 293. With regard to the calculations from these observations, *vide* Weber, *loc. cit.*

[7] *Ibid.* 1870, cxli. 1.

[8] *Ibid.* 87.

[9] *Lieb. Ann.* 1873, clxix. 388.

[10] *Pogg. Ann.* 1876, clviii. 71.

[11] *Ber. d. chem. Ges.* 1878, 381; *Nov. Acta Reg. Soc. Sc. Ups.* ser. iii. May, 1878.

[12] *Ann. Chim. Phys.* [5] 1878, xv. 242.

[13] *Ber. deut. chem. Ges.* 1882, 847.

SPECIFIC HEATS OF THE ELEMENTS.

I.	II. c	III. t	IV. Observ.	V. A	VI. Ac
Lithium	0·941	+ 64°	Rg.	Li = 7·01	6·6
Boron, crystalline[1]	0·366	+233	Wb.	B = 10·9	4·3
" "	0·5(?)	+600	,,[2]	" "	(5·45)
Beryllium	0·582	+257	N. P.	Be = 9·1	5·3
Carbon :					
(*a*) Diamond	0·459	+985	Wb.	C = 11·97	5·5
(*b*) Graphite	0·467	+978	"	" "	5·5
Sodium	0·293	− 14	Rg.	Na = 22·99	6·7
Magnesium	0·245	+ 36	Kp.	Mg = 23·94	5·9
"	0·250	+ 60	Rg.	" "	6·0
Aluminium	0·202	+ 37	Kp.	Al = 27·0	5·5
"	0·214	+ 60	Rg.	" "	5·8
Silicon, crystalline	0·203	+232	Wb.	Si = 28	5·7
Phosphorus, yellow	0·174	− 34	Rg.	P = 30·96	5·4
" "	0·189	+ 19	"	" "	5·9
" red	0·170	+ 67	"	" "	5·3
Sulphur, rhombic	0·163	+ 31	Kp.	S = 31·98	5·2
" "	0·171	+ 50	Bn.	" "	5·5
" "	0·178	+ 67	Rg.	" "	5·7
" fused	0·203[3]	+ 56	"	" "	6·5
Potassium	0·166	− 34[4]	"	K = 39·03	6·5
Calcium	0·170	+ 50	Bn.	Ca = 39·9	6·8
Chromium	0·100[5]	+ 36	Kp.	Cr = 52·4	5·2[5]
Manganese[6]	0·122	+ 55	Rg.	Mn = 54·8	6·7
Iron	0·112	+ 31	Kp.	Fe = 55·9	6·3
"	0·114	+ 58	Rg.	" "	6·4
Cobalt[7]	0·107	+ 55	"	Co = 58·6	6·3
Nickel[7]	0·108	+ 55	"	Ni = 58·6	6·4
Copper	0·0930	+ 35	Kp.	Cu = 63·2	5·9
"	0·0952	+ 58	Rg.	" "	6·0
Zinc	0·0932	+ 33	Kp.	Zn = 64·9	6·1
"	0·0935	+ 50	Bn.	" "	6·1
"	0·0955	+ 55	Rg.	" "	6·2
Gallium	0·079	+ 17[8]	Bt.	Ga = 69·9	5·5
Arsenic, amorphous	0·0758[9]	+ 45	B.W.	As = 74·9	5·7

[1] *Vide* p. 69.

[2] Hypothetical value; compare § 38.

[3] This number is too high owing to heat produced by change of state.

[4] The observation was made at temperatures between −78° and some other temperature not mentioned, possibly +10°.

[5] This number is too low, the reasons for this are given by Kopp (*loc. cit.* p. 77).

[6] It contained some silicon; a specimen containing a large amount of silicon and carbon gave $c = 0·133$.

[7] These are the smallest values obtained; specimens containing carbon gave higher numbers, *e.g.* 0·116 and 0·117.

[8] At temperatures between 23° and 12°C., and therefore for very narrow limits.

[9] The numbers obtained by Bettendorf and Wüllner are too high; *vide* Weber (*loc. cit.* p. 5).

SPECIFIC HEATS OF THE ELEMENTS—*continued.*

I.	II. c	III. t	IV. Observ.	V. A
Arsenic, crystalline .	0·0830[1]	+ 45°	B.W.	As = 74·9
,, ,, .	0·0814	+ 55	Rg.	,, ,,
,, ,, .	0·0822	+ 56	N.	,, ,,
Selenium, amorphous [2].	0·0746	− 9	Rg.	Se = 78·9
,, crystalline .	0·0745	− 5	,,	,, ,,
,, ,, .	0·0840[1]	+ 42	B.W.	,, ,,
,, ,, .	0·0861	+ 61	N.	,, ,,
,, ,, .	0·0762	+ 59	Rg.	,, ,,
Bromine, solid . .	0·0843	− 51	,,	Br = 79·76
Zirconium . . .	0·0662	+ 50	M.D.	Zr = 90·4
Molybdenum [3] . .	0·0722	+ 55	Rg.	Mo = 95·9
Ruthenium . . .	0·0611	+ 50	Bn.	Ru = 103·5
Rhodium [4] . . .	0·0580	+ 55	Rg..	Rh = 104·1
Palladium . . .	0·0593	+ 55	,,	Pd = 106·2
Silver	0·0560	+ 36	Kp.	Ag = 107·6
,, ...	0·0559	+ 50	Bn.	,, ,,
,, ...	0·0570	+ 55	Rg.	,, ,,
Cadmium . . .	0·0542	+ 37	Kp.	Cd = 111·7
,, . . .	0·0548	+ 50	Bn.	,, ,,
,, . . .	0·0567	+ 55	Rg.	,, ,,
Indium . . .	0·0570	+ 50	Bn.	In = 113·4
Tin	0·0548	+ 34	Kp.	Sn = 117·4
,, ...	0·0559	+ 50	Bn.	,, ,,
,, ...	0·0562	+ 55	Rg.	,, ,,
Antimony . . .	0·0523	+ 31	Kp.	Sb = 120
,, . . .	0·0495	+ 50	Bn.	,, ,,
,, . . .	0·0508	+ 55	Rg.	,, ,,
Iodine . . .	0·0541	+ 59	,,	I = 126·5
Tellurium . . .	0·0475	+ 36	Kp.	Te = 126·3
,, . . .	0·0474	+ 55	Rg.	,, ,,
Lanthanum . . .	0·0449	+ 50	H.	La = 138·5
Didymium . . .	0·0456	+ 50	,,	Di = 145
Cerium . . .	0·0448	+ 49	,,	Ce = 141
Tungsten . . .	0·0334	+ 55	Rg.	W = 183·6
Iridium . . .	0·0326	+ 60	,,	Ir = 192·7
Platinum . . .	0·0325	+ 36	Kp.	Pt = 194·3
,, . . .	0·0324	+ 55	Rg.	,, ,,
Gold	0·0324	+ 55	,,	Au = 196·2
Osmium . . .	0·0311	+ 60	,,	Os = 195

[1] The numbers obtained by Bettendorf and Wüllner are too high ; *vide* (*loc. cit.* p. 5).

[2] Bettendorf and Wüllner found $c = 0·095$, $A.c = 7·4$ at temperatures b + 20° and + 40° ; whilst Regnault obtained the following values $c =$ $A.c = 8·0$, at temperatures between + 18° and + 77° ; and $c = 0·1036$, A at temperatures between + 19° and + 85°. These numbers are too high, c the heat rendered latent by amorphous selenium, inasmuch as it so temperatures much below its melting point.

[3] This specimen contained carbon.

[4] Another specimen containing iridium gave $c = 0·0553$.

SPECIFIC HEATS OF THE ELEMENTS—*continued.*

I.	II. c	III. t	IV. Observ.	V. A	VI. $A.c$
Mercury [1] . . .	0·319	− 59°	Rg.	Hg = 199·8	6·4
Thallium . . .	0·0335	+ 58	,,	Tl = 203·7	6·8
Lead	0·0307	− 34	,,	Pb = 206·4	6·3
,, ...	0·0315	+ 34	Kp.	,, ,,	6·5
,, ...	0·0314	+ 55	Rg.	,, ,,	6·5
Bismuth . . .	0·0305	+ 34	Kp.	Bi = 207·5	6·3
,, . . .	0·0308	+ 55	Rg.	,, ,,	6·5
Thorium . . .	0·0276	+ 50	Ni.	Th = 232	6·4
Uranium . . .	0·0277	+ 49	Z.	U = 240	6·6

The maximum values of the atomic weights of 26 of the 49 elements contained in this table have been deduced, according to Avogadro's law, from the vapour density of at least one compound (*vide* table, pp. 37–42). This represents the smallest quantity of an element which can exist in the molecule of one of its compounds.

The numbers obtained by the application of the hypotheses of Avogadro and of Dulong and Petit agree in the majority of cases, as is shown by the tables on pp. 37–42 and 73. In the following instances, the deductions from these two hypotheses have led to the acceptance of the same atomic weights, viz., for boron, carbon, silicon, phosphorus, sulphur, chromium, zinc, gallium, arsenic, selenium, bromine, zirconium, molybdenum, cadmium, indium, tin, antimony, iodine, tellurium, tungsten, osmium, mercury, thallium, lead, bismuth, and uranium.

The atomic weights of aluminium, iron, and copper, as deduced from their specific heats, are half those deduced from the molecular weights of their compounds. Consequently, in all the compounds of these metals known in the gaseous state, we assume the existence of two atoms of the metal in the molecule. And therefore the composition of these compounds must be expressed by the following formulæ: Al_2Cl_6, Al_2Br_6, Al_2I_6, Fe_2Cl_6, and Cu_2Cl_2. Thus the deductions made from the law of specific heats in the case of these metals can be reconciled with those made from the law of Avogadro.

[1] In the solid state: liquid mercury has a somewhat higher specific heat, viz. at $t = 55°$, $c = 0·0333$ (Rg. 1840).

§ 40. The numbers in column VI. under *A.c* of the table, represent the atomic heats of the elements, *i.e.* the product of the atomic weight into the specific heat. These numbers show that the atomic heats of all the elements are not exactly identical, as is required by the law of Dulong and Petit. The numbers vary between very wide limits; in the majority of cases the atomic heat has a value varying from 6·1 to 6·5; other elements possess much lower atomic heats, as seen in the case of the elements boron, carbon, aluminium, silicon, beryllium, phosphorus, and sulphur; in some cases the atomic heat falling as low as 5·2. In the case of some other elements, such as lithium, sodium, calcium, manganese, bromine, molybdenum, and iodine, the atomic heat is above the average, rising, in fact, in some instances to 6·9. These deviations in all probability arise from impurities in the substances used; this statement certainly applies to manganese and molybdenum, and perhaps to others; the error will, of course, depend upon the nature of the impurity. Other deviations are to be attributed to errors of observation; the effect of which in the case of such substances as the alkali metals, which are manipulated with great difficulty, is considerable; and also in those cases where only small quantities of the substance can be obtained for experiment. The chief cause of the differences in the observed atomic heats is, without doubt, to be found in the following: (1) the effects of temperature upon the specific heat; (2) the effect of the physical condition of the substance. The cases in which the specific heat of an element has been determined at different temperatures prove that it increases with the temperature, and, further, the amount of this increase differs in the case of each element. Hence it follows that the atomic heats of different elements cannot at one and the same temperature be identical.

Despite the differences exhibited by the determinations already made, it is still possible that the law of Dulong and Petit is strictly true. The values for the specific heat obtained by experiment are in reality due to two constants, viz. (1) the true or absolute specific heat representing the amount of heat which is required to raise the temperature of the substance, and (2) the amount of heat required for the purposes of ex-

pansion, and also to produce changes of those functions which Clausius [1] has styled *disgregation*. It can therefore be easily understood that the apparent specific heats of some of the elements should be found greater or less than required by the law of Dulong and Petit, insomuch as the amounts of heat required to produce the changes of the 'disgregation' in each case must be different.

Although the inequality in the amount of heat required to produce molecular changes is sufficient to explain the inequalities in the atomic heats of most of the elements, it does not, however, suffice to explain the deviations exhibited by boron, carbon, beryllium, and silicon at low temperatures. Experiment points rather to the conclusion that in the case of these elements the law holds true at certain temperatures only, dependent upon the nature of the substance. Taking into consideration the observations made in the case of some elements, viz., that this law does not, in the majority of cases, hold true at temperatures approaching the melting point, and that its application ceases entirely in the case of liquids, the conclusion then becomes more forcible that the law of Dulong and Petit is true only within certain fixed limits of temperature; at any rate, this is the case with the non-metallic elements. It is characteristic of this interval of temperature that within it the specific heat is but slightly affected by change of temperature, whereas at temperatures above or below, the specific heat varies considerably with the temperature.

§ 41. Having arrived at this conclusion, it is necessary in deducing the atomic weight of an element from its specific heat to show that the latter has been determined at temperatures between which it exhibits but slight variations. This proof is obtained by determining the specific heats at several temperatures sufficiently removed from one another.

Such determinations have been made for iron, copper, zinc, silver, antimony, platinum, and mercury by Dulong and Petit; [2] for platinum by Pouillet; [3] for iron, copper, zinc, tin,

[1] Clausius, 'Ueber die Anwendung des Satzes von der Aequivalenz der Verwandlungen auf die innere Arbeit,' *Pogg. Ann.* 1862, cxvi. 73.

[2] *Ann. Chim. Phys.* [2], 1818, vii. 142. [3] *Compt. Rend.* 1836, ii. 782.

antimony, lead, and bismuth by Bède ;[1] for iron, silver, and platinum by Byström ;[2] for platinum by Weinhold ;[3] and for platinum, iridium, and gold by Violle.[4] The specific heats and the variations due to temperature obtained by these investigators exhibit certain differences, but all agree in showing the atomic heats of these elements to exhibit but slight differences, even at temperatures many hundreds and even at a thousand degrees above the boiling-point of water. The mean atomic heat of these elements was found to be some 7 units. Hence it follows that the law of Dulong and Petit holds good even at such high temperatures.

Such observations are, however, wanting for the majority of the elements. The identity of the atomic weights deduced by application of the law of specific heats with those obtained by aid of Avogadro's law, and other reasons which will be given later on, indicate that the values given in column V. of the table (§ 39) represent the true atomic weights. Consequently the temperature at which these specific heats have been determined must either be within or not far removed from the correct limits.

The undoubtedly incorrect determination of the specific heat of beryllium by Emerson Reynolds[5] makes $c = 0{\cdot}64$, corresponding to the atomic weight Be = 9·1 ($A.c = 5{\cdot}8$). (There are many reasons for regarding this as the true value for the atomic weight.) Nilson and Pettersson[6] found the specific heat of the metal equal to 0·41 at 50°, and assumed that its atomic weight was half as large again. Be = 13·7 ($A.c = 5{\cdot}6$). After Brauner[7] had pointed out that it was highly probable that the specific heat of this metal, like that of boron, carbon, and silicon, would be greatly influenced by temperature, Nilson and Pettersson confirmed the prediction by experiment. But since the variation is less than in the case of boron and carbon, and is nearly the same as Bède[8]

[1] *Fortschritte d. Physik.* 1855, ix. 379.
[2] *Ibid.* 1860, vi. 369.
[3] *Programm der h. Gewerbschule zu Chemnitz, Ostern*, 1873, 32.
[4] *Compt. Rend.* 1877, lxxxv. 543 ; 1879, lxxxix. 702.
[5] *Phil. Mag.* [5] 1877, iii. 38.
[6] *Loc. cit.* 90.
[7] *Ber. deutsch. chem. Ges.* 1878, xi. 873.
[8] *Mém. Cour. &c. de l'Acad. de Bruxelles*, xxvii.

found for iron, Nilson and Pettersson were at first inclined to retain the larger atomic weight. But iron is not suited for instituting such a comparison, as it softens long before melting, and the highest value for c observed by Nilson and Pettersson, viz., 0·58 at 257°, gives for the atomic heat $A.c = 7·9$, which is obviously too high. Hence it is at least very probable that the more correct assumption is that Be = 9·1.[1]

In all probability the atomic heats would exhibit a greater similarity if the specific heats were determined at temperatures at which they exhibit the least change.

Since the atomic heats of carbon and silicon, determined at temperatures at which their specific heats are almost constant, are lower than 6 units of heat, it is therefore possible, and not improbable, that the elements the atomic heats of which have hitherto been found to be small will retain a low atomic heat at all temperatures. Small atomic heats are exhibited by non-metallic and semi-metallic elements with small atomic weights, such as boron, carbon, silicon, phosphorus, and sulphur; and also by the metals aluminium, beryllium, and magnesium.

Should future investigation confirm the supposition that the law of specific heats is only approximately true, this would not in any way lessen its value. Inasmuch as natural laws are simply generalisations based upon observations, and hold true for those limits only within which the facts leading to their discovery or confirmation lie, the application of such a law may, therefore, be very limited without affecting its value. Boyle's or, as it is frequently styled, Marriotte's law, viz. that the density of a gas is proportional to the pressure, holds true, and then only approximately, within certain limits of temperature and pressure. This statement applies also to Avogadro's law, which is dependent upon Boyle's law, and is therefore, as is the case with the latter, true only under these conditions. Further, it is only true for temperatures far removed from that at which the gas passes into the state of liquid.

Similarly, it has been known for some time that the law of Dulong and Petit, at least in its present form, does not hold

[1] *Vide* Lothar Meyer, *Ber. deut. chem. Ges.* 1880, xiii. 1780; L. F. Nilson, *ibid.* 2035.

true for gases or liquids, and can only, as a rule, be applied to solids, at temperatures much below their melting-points. Further, Weber's experiments indicate that there is a limit of temperature below which this law no longer holds. On the other hand, it is possible for some elements, both in the solid and in the liquid state, to obey this law. Winkelmann [1] has shown that this is true of mercury, the specific heat of which, instead of increasing, appears to diminish with an increase of temperature. At present we are not in the position to state in general terms the conditions affecting the validity of this law. In order that this may be done, it is necessary that investigations embracing a large number of elements should be made, to ascertain the influence of temperature upon the apparent specific heats. Such investigations, as pointed out by Weber (*loc. cit.*), would be of great value to the study of physics.

§ 42. The specific heat of atoms is apparently unaltered by combination, and consequently the molecular weight of a compound in the solid state possesses a specific heat, which is made up of the sum of the specific heats of the atoms contained in the compound.[2]

Thus, for example, the specific heat of lead iodide as determined by Regnault is 0·0427, and that of lead bromide 0·0533. If these numbers are multiplied by the molecular weights [3] of these compounds, viz. 459·5 and 365·9 respectively, then the products obtained, viz. 19·6 and 19·5, represent the specific heats of these molecules or their molecular heats. The sums of the atomic heats of the atoms contained in these compounds are, according to the table, § 39 :

$$\text{For lead iodide} \quad 6{\cdot}5 + 2 \times 6{\cdot}8 = 20{\cdot}1.$$
$$\text{For lead bromide} \quad 6{\cdot}5 + 2 \times 6{\cdot}7 = 19{\cdot}9.$$

[1] *Pogg. Ann.* 1876, clix. 152.

[2] An account of the part taken by different investigators in establishing this law, especially by Regnault, De la Rive and Marcet, H. Schröder, Woestyn, Garnier, Bancalari, Cannizzaro, and others, is to be found in the historical introduction to Kopp's complete work on this subject (*Lieb. Ann.* 1864; Suppl.-Bd. iii. 1, &c.)

[3] These molecular weights are hypothetical; we may substitute for them double the quantities Pb_2I_4, and Pb_2Br_4, or any other multiples, without in the least affecting the point in question.

Thus, supposing the atomic heats of bromine and iodine were unknown, they might be deduced approximately from the molecular heats of the bromide and iodide by subtracting from them the atomic heat of the lead contained in these compounds. The remainder, obtained in this manner, represents the atomic heats of bromine or iodine.

Performing this calculation we obtain the following results:

$$19{\cdot}6 - 6{\cdot}5 = 13{\cdot}1 = 2 \times 6{\cdot}55 \text{ for iodine.}$$
$$19{\cdot}5 - 6{\cdot}5 = 13{\cdot}0 = 2 \times 6{\cdot}5 \text{ for bromine.}$$

These values differ but slightly from those obtained by direct experiment, viz. 6·8 for iodine and 6·7 for bromine.

In a similar manner, the specific heat of lead chloride, found by Regnault to be 0·0644, may be used to determine that of chlorine. An atom or 206·4 parts by weight of lead yield 277·1 parts by weight of lead chloride, and multiplying the specific heat by this number we obtain 18·4 as the molecular heat of the chloride (277·1 × 0·0644). Subtracting from this the atomic heat of lead, we then obtain,

$$18{\cdot}4 - 6{\cdot}5 = 11{\cdot}9 = 2 \times 5{\cdot}95,$$

$2 \times 5{\cdot}95$ as the specific heat of 70·7 parts by weight of chlorine.

Consequently accepting the atomic weight of chlorine as 35·37, as deduced from the vapour density of chlorine compounds, then its atomic heat is 5·95, or very nearly 6. The specific heats of other chlorine compounds give approximately the same number.

Hence it follows that the atomic weight of chlorine, Cl = 35·37, as determined by the aid of Avogadro's law, satisfies the conditions of the law of Dulong and Petit.

Calculations of this character have often been applied successfully. In fact, Regnault has obtained by this means values for the specific heats of sodium, potassium, and lithium from those of their compounds, which his later determinations with the metals themselves served to confirm. This statement also applies to magnesium and calcium; but such direct confirmation is still wanting in the case of barium and strontium.

For such calculations of the specific heat of an element it is

not absolutely necessary that its specific heat in all its compounds should be known; it is sufficient to determine the changes exhibited by the specific heat of a compound when the element of unknown specific heat is replaced by one the specific heat of which has been determined. Thus, for example, the interchange of lead for barium, calcium, or strontium in a compound does not affect its molecular heat. From this it follows that the amounts of these metals which replace one another possess the same specific heats, and therefore the amounts of these three light metals, which can so replace an atom or 206·4 parts by weight of lead, represent the atoms of these metals.

In illustration of this statement the following instances may be cited: (1) 266·25 parts by weight of cerussite contain 206·4 parts by weight of lead, combined with 11·97 of carbon and 47·88 of oxygen; (2) 99·75 parts by weight of arragonite or calc spar contain the same amounts of these latter elements combined with 39·9 parts of calcium; (3) 147·05 parts by weight of strontianite contain them united with 87·2 parts of strontium; and finally they occur in 196·75 parts by weight of witherite united with 136·9 parts of barium. These quantities when multiplied by the specific heats [1] of the compounds which they represent, give approximately the same product, hence the molecular heats of these compounds are almost identical, as shown by the following numbers:

Calc spar, or arragonite	$99{\cdot}75 \times 0{\cdot}206 = 20{\cdot}6$
Strontianite . .	$147{\cdot}05 \times 0{\cdot}145 = 21{\cdot}3$
Witherite . . .	$196{\cdot}75 \times 0{\cdot}109 = 21{\cdot}4$
Cerussite . . .	$266{\cdot}25 \times 0{\cdot}080 = 21{\cdot}3$

Without a knowledge of the specific heats of the other constituents of these compounds we may conclude from the above result that the quantities of calcium, strontium, barium, and lead which replace one another possess the same specific heat. Further, just as 206·4 parts by weight of lead represent an atom possessing the normal atomic heat of 6, so do the above quantities of calcium, strontium and barium, represent

[1] These values for the specific heats are the means of the determinations of Neumann, Regnault, and Kopp. *Vide* Kopp (*loc. cit.* 295).

atoms of these elements. This conclusion has been confirmed in the case of calcium by Bunsen's direct determination of its specific heat.

In this manner the atomic weights of a number of elements may be determined. The accuracy of the results increases with the number of compounds from which such deductions have been made. Of atomic weights calculated in this manner the following are in all probability the most accurate. (These numbers are corrected, as before, from the best analytical determinations.)

Chlorine, Cl = 35·37	Rubidium, Rb = 85·2
Titanium, Ti = 48·0	Strontium, Sr = 87·2
Chromium, Cr = 52·45	Barium, Ba = 136·86

These quantities of each of these elements possess a specific heat of 6 in their compounds, and therefore obey the law of Dulong and Petit. In the case of chlorine, titanium, and chromium, moreover, the atomic weights so obtained agree with those deduced from the vapour density of some of their compounds.

This method of deducing the atomic heat, and consequently atomic weight, of an element from the specific heat of its compounds, is only reliable when the number of atoms contained in the compounds is small, and, further, when all the elements obey the law of Dulong and Petit. Should this not be the case the results obtained are untrustworthy. The author,[1] for example, obtained the atomic weight 180 for uranium from the specific heat of uranous oxide, whereas J. Donath[2] obtains the value 120 from the specific heat of urano-uranic oxide. Both of these values are in all probability incorrect, for the atomic heat of the elements cannot be deduced with certainty from the specific heat of their oxides until the influence of temperature on these specific heats has been ascertained within very wide limits.

§ 43. The deductions made from the laws of Avogadro and of Dulong and Petit do not agree in the case of all elements. If this were so in all cases, and the atoms of all

[1] *Lieb. Ann.* 1870; Suppl.-Bd. vii. 363.
[2] *Ber. deut. chem. Ges.* 1879, 742.

elements retained in their compounds the specific heats required by the law of Dulong and Petit, then the quotient obtained by dividing the molecular heat of a compound by the number of elements contained in it should be very nearly 6, which represents according to this law the specific heat of an atom.

The observations made at temperatures between 0° and 100° give this number as quotient, at all events, for compounds of those elements which obey the law of Dulong and Petit in the free state. The quotients are smaller than 6 in the case of the compounds of those elements such as boron, beryllium, carbon, and silicon, which do not obey this law at temperatures below 100°, and also for the compounds of elements such as phosphorus, sulphur, aluminium, and magnesium, which in the free state do not exactly conform to this law. Similar deviations are exhibited by the compounds of some of those elements, the specific heats of which, in a solid state, it has hitherto proved impossible to determine; the atomic weights of these elements have, however, been determined by the aid of Avogadro's law. Special illustrations of this exceptional behaviour are afforded by the elements oxygen, hydrogen, nitrogen, and fluorine. Many suggestions have been made with a view to explain these deviations. H. Schröder,[1] in 1840, stated that the capacity for heat of a compound must represent the sum of the capacities of its constituents, but considered it was necessary in addition to accept the conclusion that the atomic heat of one and the same element could vary in different compounds, and may be specially influenced by the state of condensation in which the atom occurs. H. Kopp[2] afterwards concluded, from a large series of observations, that the specific heat of an atom remains approximately the same, whether the atom is contained in a simple or compound body, so long as the substance is solid and the temperature of observation is sufficiently below that of its melting-point.

Starting from this conclusion, he calculated the atomic

[1] *Pogg. Ann.* l. 553.

[2] *Loc. cit.* cxxvi. 368; Suppl.-Bd. iii. 314, &c. *Ibid.* §§ 82–89, 290–298, and in §§ 103–110, will be found a complete summary, as far as the year 1865, of the reliable conclusions from experiments upon the specific heat of elements and compounds.

heats of elements, the specific heats of which in the isolated state had not been determined. These values were obtained by deducting from the capacities for heat of their compounds the capacities of those elements contained in them, the specific heats of which had been determined directly.[1]

In this way the following numbers were obtained :

	Atomic weights	Atomic heats
Hydrogen, H	= 1·0 .	2·3 (nearly)
Oxygen, O	= 15·96 .	4·0 ,,
Fluorine, F	= 19·1 .	5·0 ,,
Nitrogen, N	= 14·01	from 5 to 5·5

Kopp[2] leaves it an open question whether nitrogen obeys the law entirely or only approximately. Inasmuch as the nitrates having the formula RNO_3 (in which R represents a metal for which the law holds true) exhibit a much smaller molecular heat than the chlorates $RClO_3$, metaphosphates RPO_3, and metaarsenates $RAsO_3$; further, the molecular heats of such nitrates is not much greater than those of the carbonates RCO_3, or the silicates $RSiO_3$. Hence it appears that the atomic heat of nitrogen can scarcely be greater, but is probably less than that of phosphorus.

Kopp has also calculated, from the molecular heats of their compounds, the atomic heats of the following elements, and has thus obtained numbers which agree well with those obtained for the element in the free state at 0–100° :

	Atomic weights	Atomic heats
Boron, B	= 10·9 .	2·7 (nearly)
Carbon, C	= 11·97 .	1·8
Silicon, Si	= 28·0 .	4·0
Phosphorus, P	= 30·96 .	5.4
Sulphur, S	= 31·98 .	5·4

The molecular heats of the compounds of aluminium, magnesium, and beryllium are smaller than those of the corresponding compounds of other metals; a fact which is in accord with the small atomic heats of these metals.

The specific heats of the majority of compounds hitherto investigated agree well with those deduced by the aid of

[1] *Loc. cit.* 321. [2] *Loc. cit.* 323.

Kopp's hypotheses.[1] In some cases, however, the calculated and experimental numbers differ to such an extent that the deviations cannot be regarded as due to experimental errors.

Since Weber has shown that the specific heats of boron, carbon, and silicon are greatly influenced by the temperature, and Nilson and Pettersson have proved the same for beryllium, it is probable that the specific heats of some of the above-mentioned elements may be similarly influenced.

Further, the allotropic modifications of an element, *e.g.* diamond and graphite, have been shown to possess different specific heats; and it may therefore be assumed that the specific heat of an element, and the influence of temperature upon it, will vary in different compounds. Hence the atomic heats accepted by Kopp must be regarded as the means only, from which the real values, in some cases at least, may differ considerably. It is not improbable that these observed deviations may, as suggested by Schröder, be related to the density of the compounds; observations hitherto made do not, however, suffice for the solution of this question.

§ 44. All those elements possessing a smaller atomic heat than the majority, although they differ in other properties, have one property in common, viz. the possession of a small atomic weight. In the case of those elements exhibiting marked deviations from the majority, their atomic weights are less than that of fluorine (19), and the atomic weights of those elements which approximate more closely to the general law are not greater than that of chlorine (35·37). On the other hand, it appears that all elements the atomic weights of which are greater than 35·37, have between 0° and 100° atomic heats of at least six units. To this, however, sodium and lithium are exceptions, for although their atomic weights are small yet their atomic heats are,[2] in all probability, some-

[1] *Loc. cit.* 330.

[2] Compare Pape's criticism, *Pogg. Ann.* 1863, cxx. 579. It is worthy of note that, according to Regnault's own determinations, the molecular heats of the compounds of lithium are less than those of the corresponding sodium compounds, and these again less than those of potassium. Hence the atomic heats of lithium and sodium should be less than those found by Regnault; these differences would not, however, be sufficient to influence their subservience to the law of Dulong and Petit.

what larger than 6. The three other metals, viz. beryllium, magnesium, and aluminium, with atomic weights less than 35, have both in the free state and in their compounds atomic heats smaller than those possessed by the majority of the elements.[1]

But those elements with small atomic weights, to which the law of Dulong and Petit applies only approximately or not at all, between 0° and 100° C., belong to a large extent to the elements which pre-eminently form gaseous or easily volatile compounds, and hence their atomic weights may be determined by the aid of Avogadro's law. In this way both methods supplement each other most satisfactorily.

The atomic weights deduced from the determinations of the specific heats at temperatures below 100° may be without hesitation accepted for all elements possessing large atomic weights and consequently relatively small specific heats. Further, the atomic weights determined by this method may also be accepted in the case of those metals which have been shown to obey the law of Dulong and Petit at temperatures below 100°. The atomic weights determined in this manner, in the case of some metals and of the metalloids with large atomic weights, agree, as has been shown already, with the values deduced from the determination of the vapour density of their compounds.

The conclusion drawn from the determination of the specific heat within narrow limits of temperature is, as a rule, untrustworthy in the case of elements with small atomic weights, and consequently relatively large specific heats. In cases where Avogadro's law affords no clue for the determination of the atomic weight, it is necessary that the influence of temperature on the specific heats of these elements should be investigated; and only those values of the specific heat which are almost identical within a wide range of temperatures should be used in fixing the atomic weight.

[1] Regnault in his early investigations observed that, in the cases of analogous and especially of isomorphous compounds, the molecular heat is higher the greater the molecular weight. *Vide Ann. Chem. Phys.* [3], 1841, i. 198; 1843, ix. 341.

This rule is entirely empirical and cannot at present be explained on theoretical grounds. This fact does not, however, prevent it being used; since, in the matter of specific heats, we are at present entirely dependent upon experience, which has often brought and may still continue to bring to light facts in direct contradiction to our theoretical views, and thus necessitate changes in our theories.

§ 45. A comparison of the atomic weights determined by the aid of the law of Dulong and Petit with those which have been obtained by the application of Avogadro's law, shows that there is a complete agreement in the results of the two methods in the case of all elements the specific heats of which have been determined in the elementary and solid state. The atomic heats of hydrogen and oxygen (accepting the atomic weights deduced from their densities), calculated from the molecular heats of their compounds, are much smaller than required by the law of Dulong and Petit. This may probably arise from the specific heats of these elements, at temperatures below 100°, being influenced by temperature, in a similar manner to those of boron, carbon, beryllium, and silicon. The atomic heats of all other elements hitherto investigated are about six units, when the atomic weights used are those which have been determined by the aid of Avogadro's law.

The following table contains all those elements the atomic weights of which have been determined by these two methods. The first column contains the names of the elements; the second gives the atomic weights arranged according to their numerical values, the atomic weight of hydrogen being taken as unit. The sign Av attached to the atomic weights indicates that the two methods give the same value for the atomic weights. The sign (Av) indicates that the smallest quantity of an element found in the molecule is a multiple of the atomic weight. The third column contains the mean of the values found for the specific heats, and in the fourth column the atomic heats are given. In those cases where the atomic heats have not been determined directly, but by calculation from the specific heat of the compounds, the resulting numbers are placed in brackets.

ATOMIC WEIGHTS AND ATOMIC HEATS.

I. Element	II. Atomic Weights	III. Spec. Ht.	IV. Atom. Ht.
Hydrogen	H = 1 Av.	(2·3)	(2·3)
Lithium	Li = 7·01	0·941	6·6
Beryllium	Be = 9·1	0·58	5·3
Boron	B = 10·9 Av.	0·5 ?	5·5
Carbon	C = 11·97 Av.	0·46	5·5
Nitrogen	N = 14·01 Av.	(0·36)	(5)
Oxygen	O = 15·96 Av.	(0·25)	(4)
Fluorine	F = 19·06 Av.	(0·26)	(5)
Sodium	Na = 22·99	0·29	6·7
Magnesium	Mg = 23·94	0·25	6·0
Aluminium	Al = 27·0 (Av.)	0·21	5·5
Silicon	Si = 28 Av.	0·16	5·7
Phosphorus	P = 30·96 Av.	0·17	5·3
Sulphur	S = 31·98 Av.	0·16	5·1
Chlorine	Cl = 35·37 Av.	(0·18)	(6·4)
Potassium	K = 39·03	0·17	6·5
Calcium	Ca = 39·9	0·17	6·8
Titanium	Ti = 48 Av.	(0·13)	(6·4)
Vanadium	V = 51·1 Av.	?	?
Chromium	Cr = 52·4 Av.	(0·12)	(6·4)
Manganese	Mn = 54·8	0·12	6·7
Iron	Fe = 55·9 (Av.)	0·11	6·3
Nickel	Ni = 58·6	0·11	6·4
Cobalt	Co = 58·6	0·11	6·4
Copper	Cu = 63·2 (Av.)	0·094	6·1
Zinc	Zn = 64·9 Av.	0·094	6·1
Gallium	Ga = 69·9	0·079	5·5
Arsenic	As = 74·9 Av.	0·081	6·1
Selenium	Se = 78·9 Av.	0·075	5·8
Bromine	Br = 79·76 Av.	0·084	6·7
Rubidium	Rb = 85·2	(0·077)	(6·4)
Strontium	Sr = 87·2	(0·074)	6·4
Zirconium	Zr = 90·4 Av.	0·066	6·0
Niobium	Nb = 94 Av.	?	?
Molybdenum	Mo = 95·9 Av.	0·072	6·9
Ruthenium	Ru = 103·5	0·061	6·3
Rhodium	Rh = 104·1	0·058	6·0
Palladium	Pd = 106·2	0·059	6·3
Silver	Ag = 107·66	0·056	6·0
Cadmium	Cd = 111·7 Av.	0·057	6·3
Indium	In = 113·4	0·057	6·5
Tin	Sn = 117·4 Av.	0·056	6·6
Antimony	Sb = 120 Av.	0·051	6·1
Tellurium	Te = 126·3 Av.	0·047	6·0
Iodine	I = 126·53 Av.	0·054	6·8
Barium	Ba = 136·86	(0·047)	(6·4)
Lanthanum	La = 138·5	0·045	6·2
Didymium	Di = 145	0·046	6·6
Cerium	Ce = 141	0·645	6·3
Tantalum	Ta = 182 Av.	?	?
Tungsten	W = 184 Av.	0·033	6·1
Iridium	Ir = 192·5	0·033	6·3
Platinum	Pt = 194·3	0·033	6·3
Gold	Au = 196·2	0·032	6·4

ATOMIC WEIGHTS AND ATOMIC HEATS—*continued.*

I. Element	II. Atomic Weights	III. Spec. Ht.	IV. Atom. Ht.
Osmium	Os = 195 Av.	0·031	6·0
Mercury	Hg = 199·8 Av.	0·032	6·3
Thallium	Tl = 203·7 Av.	0·034	6·8
Lead	Pb = 206·4 Av.	0·031	6·5
Bismuth	Bi = 207·5 Av.	0·031	6·3
Thorium	Th = 232	0·028	6·4
Uranium	U = 240 Av.	0·028	6·6

An account is given in this table of nearly all the known elements, but the following are omitted: the metals contained in gadolinite, and also caesium, scandium, norwegium, and some other newly discovered bodies the elementary nature of which is still doubtful. The physical and chemical nature of caesium, together with its resemblance to potassium and rubidium, show that its atomic weight has been correctly determined, viz. Cs = 132·7. Further, the atomic weight, 44, assigned to scandium, a metal analogous to aluminium, is in all probability correct. The atomic weights of the other elements mentioned above cannot yet be regarded as fixed.

§ 46. A remarkable relationship is exhibited by the specific heats of elements in the solid state, and their specific heats in the gaseous state at constant volume. This is shown in the following table, in the case of some few elements the specific and atomic heats of which have been determined in the solid and gaseous states. The numbers representing the specific heats of the gases at constant volume are those calculated by Clausius.[1] The specific heat of mercury in the state of vapour at constant volume has been calculated by the author, by multiplying its specific heat = 0·1027 (Kundt and Warburg)[2] by its vapour density, viz. 6·98.

This table shows that, with the exception of hydrogen and oxygen, which do not obey the law of Dulong and Petit, the elements possess, in the solid state, specific or atomic heats

[1] *Ann. Chem. Pharm.* 1861, cxviii. 118. These values will be found to be slightly higher if those numbers are used which, according to Röntgen (*Pogg. Ann.* 1873, cxlviii. 603) express the relationship between the specific heat for constant pressure to that for constant volume.

[2] *Pogg. Ann.* 1876, clvii. 368.

	Solid		Gaseous		Ratio
	c	$A.c$	c	$A.c$	
Hydrogen . . .	2·3	2·3	2·41	2·4	1 : 1
Oxygen . . .	0·25	4·0	0·156	2·5	1·6 : 1
Nitrogen . . .	0·36	5·0	0·173	2·4	2 : 1
Chlorine . . .	0·18	6·4	0·093	3·3	2 : 1
Bromine . . .	0·084	6·7	0·042	3·4	2 : 1
Mercury . . .	0·032	6·4	0·015	3·0	2 : 1

twice as great as their specific or atomic heats in the gaseous state. It is not at present apparent why this should be the case, yet it can scarcely be considered as due to chance.

Should it be found that the specific heats of hydrogen and oxygen, in their solid compounds, vary with the temperature in a manner similar to that of carbon, then it is highly probable that their specific heats at high temperatures will exhibit this same relationship.

Futile attempts have been repeatedly made to show that the specific heats of gaseous compounds are subservient to law, just as those of solid bodies are subservient to the laws of Dulong and Petit, and to the extension of Neumann's law proposed by Regnault and Kopp. The futility of these attempts is not surprising, inasmuch as the specific heats of some gases vary considerably with the temperature, whilst in other cases temperature has no apparent influence.[1]

§ 47. The agreement exhibited in the majority of cases by the atomic weights deduced from two such different properties, viz. from the vapour density and the specific heat, shows that these values must be strictly analogous. And therefore these values possess, for chemical statics, a real and not imaginary signification.

These atomic weights will always retain this signification, whether the future may or may not show them capable of further simplification. The extent of their importance cannot at present be fully realised; but from a more thorough consideration it is seen that these two properties, used to determine the atomic weights, are nearly related to one another, inasmuch as a close analogy is seen to exist between the mole-

[1] Regnault, *Relation des Expér.* ii. 128 and 162; Eilhardt Wiedemann, *Pogg. Ann.* 1876, clvii. 1.

cular weights determined by the aid of Avogadro's hypothesis and the atomic weights determined by the aid of the hypotheses of Dulong and Petit.

It has been already pointed out (§ 14) that the present kinetic theory of gases, based upon Avogadro's hypothesis, shows that the molecular weights $\mathfrak{M}_1$ and $\mathfrak{M}_2$ of any two gases, under the same conditions of temperature and pressure, are related as follows :

$$\tfrac{1}{2}\mathfrak{M}u^2 = \tfrac{1}{2}\mathfrak{M}_1 u_1^2.$$

Hence, according to Avogadro's hypothesis, the molecules may be defined as those particles of matter the kinetic energy due to the rectilinear motion of which is, under the same conditions of temperature and pressure, the same for all gases, and is affected alike for equal increments of temperature.

Similarly the thermal atoms may be defined as those units of mass which in the solid state require the same amount of heat, or to which equal amounts of energy must be imparted, in order to raise their temperature through an equal number of degrees.

Thus a remarkable analogy is established between the molecular weights, deduced by Avogadro's hypothesis from the properties of matter in the gaseous state, and the atomic weights determined by the law of Dulong and Petit from a property of matter in the solid state. This analogy is, without doubt, due to the fact that these values, determined by such apparently different methods, represent those particles of matter which possess a motion of a fixed and independent character. In the case of the molecules of a gas this motion is rectilinear, and is the origin of the pressure exerted by gases ; whereas, in the case of solids, although the motion is probably similar, yet the path which an atom can traverse, before and after collision with a neighbouring atom, is much more limited.

§ 48. This conception, however, leaves some difficulties to be removed, *e.g.* it does not explain how it is that some elements possess a small atomic heat at low temperatures. If these elements possessed small atomic heats in the isolated state only, and not in their compounds also, then such excep-

tions to the law might be explained by the supposition that the molecules of these elements consist of several atoms, united closely and immovably to one another, performing a similar part to that played in the case of other elements by the single and independently moving atoms. This explanation cannot, however, be accepted, since these elements possess a low specific heat even in those of their compounds which can only contain one of their atoms.

Prior to our knowledge of the influence of temperature upon the specific heats of these elements, H. Kopp proposed a hypothesis to explain these remarkable exceptions. The apparent anomaly in the behaviour of, in other respects analogous substances, was compared with similar differences in the properties of compound bodies; and thus the difficulties were to some extent apparently removed. Kopp, reviving the doubts often expressed as to the simplicity of the elementary atoms, supposes them to be in reality composed of atoms of a still higher order, although they have as yet resisted attempts to decompose them. Further, that the atoms of those elements possessing small specific heats contain a smaller number of such atoms than the atoms of those elements which have a high specific heat. Thus the atom of carbon or silicon should be related to that of tin in the same manner that potassium is to ammonium; for, in accordance with other analogies, the compounds of ammonium should possess larger molecular heats than those of potassium.

The discovery of the variation of the specific heat of carbon and of other elements with the temperature necessitates some alteration in this hypothesis of Kopp's. This end would be attained by supposing that elementary atoms are composed of still smaller parts, which we may style particles, and that at low temperatures the motion of these particles is that of a single system; at higher temperatures this system is resolved into others containing a smaller number of particles; and finally, at still higher temperatures, this resolution takes place to such an extent that each particle moves freely and independently. Therefore, according to this hypothesis, at temperatures at which the atoms do not obey the

law of Dulong and Petit, the particles do not move singly, but in groups of several such particles, each of which requires the same amount of heat to raise its temperature through one degree as is required by the single particle of an atom subservient to this law. For example, an atom of carbon, in the form of diamond, possessing at $-50°$ C. an atomic heat of 0·76, contains half the number of groups of particles which it contains at 27·7°, at which temperature its atomic heat is twice as large, viz. 1·52. The different groups are not of necessity twice as large, but must, on an average, contain twice as many particles at $-50°$ as they contain at $+27·7°$.

§ 49. Viewed in this light, the exceptions to the law of Dulong and Petit form a parallel to the instances described in §§ 31–33 of vapours subject to dissociation. For example, as the vapour of the so-called amylene hydrobromide consists, at temperatures below 180°, of molecules having the composition $C_5H_{11}Br = 150·61$; and above 300°, of two species of molecules, viz. $C_5H_{10} = 69·85$, and $HBr = 80·76$, and between these two temperatures of all three species of molecules, each possessing its own independent motion. So, in accordance with the above hypothesis, carbon, in the solid state, consists, at a very low temperature, $t_0°$, of a number of independently moving particles, having a mass of $C = 11·97$. At a higher temperature, $t_1°$, these particles are resolved into smaller ones having a mass $\frac{1}{2}C = 5·985$; and at $t_2°$ into those of a mass $\frac{1}{3}C = 3·99$, &c. At temperatures between $t_0°$ and $t_1°$ particles of the masses C and $\frac{1}{2}C$ respectively would exist side by side; and similarly, at temperatures between $t_1°$ and $t_2°$, the masses of the particles would be $\frac{1}{2}C$ and $\frac{1}{3}C$. In the dissociated vapours of amylene hydrobromide each molecule possesses the same kinetic energy which the entire molecule itself would have, supposing no decomposition to have taken place. And hence a decomposition which would double the number of molecules must increase the energy to the same extent. Hence, in order, under constant pressure, to produce an increase in temperature of 1°, each molecule will, after dissociation, require as great an increase in its kinetic energy, or as much heat transferred to it, as was required before the dissociation had taken place. And consequently the whole

mass of the gas will require after dissociation twice as much heat to raise its temperature through 1° as was required before, since the number of molecules has been doubled by the dissociation. Thus, according to the above hypothesis, in order to raise the temperature of carbon through 1°, after the decomposition of its so-called atoms into twice or thrice the number of particles, the energy of these particles must be increased to twice or thrice the amounts required before the decomposition. Thus the observations of Weber on the specific heat of carbon are to some extent explained.

Opposed to the acceptance of this explanation is the following weighty consideration: Kundt and Warburg conclude from their experiments, described in § 27, that there is no internal motion in the atom of mercury, but that the atom moves as a single solid mass. This is probably true of other elements.

IV.

DETERMINATION OF ATOMIC WEIGHT BY MEANS OF ISOMORPHISM.

§ 50. Where sufficient observations have not been made to permit of the use of one or other of the previously mentioned methods, a third means of determining the atomic weight is found in the law of isomorphism, which was discovered by E. Mitscherlich almost contemporaneously with the promulgation of the law of specific heat. The atomic weight of an element cannot be determined by the preceding methods unless we are acquainted with one of its compounds in the gaseous state, or with its specific heat. But if this element is capable of replacing another (the atomic weight of which has been determined by either of the above methods) in any compound, without changing the crystalline form, the atomic weight is represented by that quantity which can so replace an atom of the other element in such a compound.

These mutually replaceable quantities of isomorphous elements have, in numerous cases, been shown to be, as a rule, identical with the atomic weights calculated according to the hypotheses of Avogadro and of Dulong and Petit.

It has been frequently observed that bodies having a different composition often exhibit identical, or almost identical, crystalline forms.

In order to explain this phenomenon, it was assumed that certain substances possessed the property of compelling other bodies to assume their crystalline form when they crystallised together; they were, indeed, supposed to be capable of exerting this influence, even when they were present in very small quantities. Thus, for example, the numerous carbonates occurring in nature in the same crystalline form as calc spar were all believed to owe their form to a certain quantity of

calc spar which they were supposed to contain. But calcium carbonate, occurring in the form of arragonite, was supposed to contain a certain amount of strontium carbonate, to which its form was due. Hence, although calcium carbonate appeared to have the power of imparting its crystalline form to the carbonates of magnesium, manganese, iron, and zinc, strontium carbonate had the property of causing calcium carbonate to assume its peculiar crystalline form.

This explanation of similar crystalline form for dissimilar composition was superseded by the one given in 1819 by Eilhardt Mitscherlich,[1] which was soon generally acknowledged to be correct.

In an investigation of the salts of phosphoric and arsenic acids, Mitscherlich found that those salts of the two acids which contain the same number of atoms in the molecule possess identical, or very similar, crystalline form. In order to investigate this remarkable relation more closely, he studied the laws and methods of crystallography[2] under the guidance of his friend, G. Rose, and found that the corresponding salts of both acids have identical, and not merely similar, crystalline form. He pursued this discovery further, and showed that the sulphates of different metals, *e.g.* of iron and copper (the so-called vitriols), which crystallise in different forms, contain different amounts of water of crystallisation, and consequently do not contain the same number of atoms. But when these salts crystallise together, they both assume the same crystalline form, and then both unite with the amount of water of crystallisation corresponding to this form. Hence they only exhibit identical crystalline form when they contain an equal number of atoms.

At first Mitscherlich believed that it was only the number, and not the nature, of the atoms which determined the crystalline form. But in the course of his investigations, which were carried out in the laboratory of Berzelius, he soon found that the nature of the atoms is of essential importance. He found that there are certain groups of elements, the

[1] *Abhandl. d. Berl. Akad.* Dec. 9, 1819; *Ann. Chim. Phys.* 1820, xiv. 172.

[2] The active part which Rose took in these investigations is described in *Zeitschrift d. deutschen geologischen Gesellsch.* 1865, 621.

members of which can, by uniting with the same number of atoms of one or more other elements, form compounds having identical crystalline form.[1]

Mitscherlich called the elements belonging to such a group isomorphous. But at the same time he recognised the fact that the compounds of these elements, with the same number of atoms of other elements, need not necessarily exhibit similar crystalline form, except when there is a similarity in the arrangement of the atoms in the compounds. He found that, under different conditions, sodium hydrogen phosphate has the power of assuming two different crystalline forms, having the same composition; and, arguing from analogy, he concluded that the difference in form between arragonite and calc spar, formerly ascribed to admixture with foreign matter, was in reality due to the same property. Having discovered numerous other instances of a similar character, Mitscherlich proposed to describe these phenomena by the terms di-, tri-, and polymorphism. In 1821 he formulated his doctrine thus:[2] an equal number of atoms similarly combined produces similarity of crystalline form; similarity of crystalline form is independent of the chemical nature of the atoms, and is only determined by their number and arrangement.

The chemical nature of the elements influences the crystalline form merely by determining the number and the arrangement of the atoms.

§ 51. Mitscherlich's discovery offered a very valuable means of determining the number of atoms united to form a compound, and also the weight of each individual particle. Berzelius, perceiving at once the true value of this great discovery, made use of isomorphism in determining the atomic weights, and placed more faith in these numbers than in those which had been deduced from the vapour density and specific heat determinations. The atomic weights of most of the elements were determined by Berzelius according to their chemical behaviour and analogies, and were even, to a certain extent, chosen arbitrarily, in such a way that the quantities of the elements which could replace each other without any

[1] *Kongl. Vetenskaps Acad. Handl. ar* 1821; *Ann. Chim. Phys.* 1822, xix. 350.
[2] *Loc. cit.* 419.

alteration in crystalline form, represented an equal number of atoms. In certain instances where this was not the case Berzelius altered his views, calling those compounds isomorphous which contained an equal number of atoms in the molecule. But he was equally unsuccessful in definitely settling the atomic weights by means of this hypothesis; in as much as the zealous investigation of isomorphism by Mitscherlich, and afterwards by other chemists, compelled him to alter once more the atomic weights he had previously adopted. Hence it appears that isomorphism though a valuable is not an entirely trustworthy means of determining the atomic weight.

§ 52. There are several reasons why such uncertainty in the conclusions deduced from isomorphism should exist. In the first place, it is by no means a rare occurrence for compounds to exhibit identical crystalline form when they contain a different number of atoms. A definite crystalline form is not necessarily produced by a similar arrangement of the atoms. It is generally very difficult, and sometimes almost impossible, to separate those cases in which a certain form is produced by similar arrangement of an equal number of atoms from those instances in which the similarity in number and arrangement is not accompanied by identity of crystalline form. In order to facilitate this separation, the property of different substances to crystallise together (already studied by Mitscherlich) has been taken as the true characteristic of isomorphism, *i.e.* identity of form for similar atomic arrangement.

Those substances are considered to be isomorphous which crystallise together, and enter in varying quantities as constituents into the composition of one and the same crystal. This limitation of the notion of isomorphism agrees pretty closely with Kopp's[1] view that bodies should only be regarded as isomorphous when they contain a similar number of atoms and having similar crystalline form, also occupy equal, or approximately equal, spaces, or have equal 'atomic,' or, more correctly speaking, molecular volumes.

[1] *Ueber Atomvolum, Isomorphismus und specifisches Gewicht, Habilitationsschrift*, Giessen, 1841; *Lieb. Ann.* xxxvi. 1. See also *Ber. d. deut. chem. Ges.* 1879, 868.

But these conditions are fulfilled by many substances in the molecules of which the existence of an equal number of atoms cannot be assumed. There are, on the contrary, a number of compounds in which individual atoms of certain elements can be replaced by groups of several atoms without altering the crystalline form of the compound. To such cases Th. Scheerer has applied the term polymeric isomorphism.[1]

The salts of potassium and ammonium offer a striking example of polymeric isomorphism. Mitscherlich in his first treatise[2] had already pointed out as an obvious fact that the corresponding potassium and ammonium salts of the same acid exhibit the same crystalline form when the ammonium salt contains 'two proportions of water of crystallisation.'

But since Mitscherlich at this time assumed with Berzelius the presence of oxygen in nitrogen and in ammonia, he expressed the mutually replaceable isomorphous quantities, *e.g.* the sulphates of both bases by the formulæ :

$$\ddot{K}\dddot{S}_2 \text{ and } 2\,\dot{N}H_6\,\dddot{S}Aq^2,$$
$$\text{or } KO_2.2SO_3 \text{ and } 2NOH_6.SO_3.2H_2O,$$

which contain an approximately equal number of atoms.

But later, when nitrogen was again regarded as a simple body, and when Berzelius, in consequence of Mitscherlich's later researches on isomorphism had reduced the atomic weights of the metals to half their former value and had introduced ammonium as the analogue of potassium, the similarity between the two formulæ increased, viz. $KO.SO_3$ and $\dot{N}H_4O.SO_3$.

Now that the atomic weight of potassium has been halved in accordance with the law of Dulong and Petit, the formulæ are written K_2SO_4 and $(NH_4)_2SO_4$. But even in this case two atoms are replaced by ten without altering the crystalline form of the compound.

If in these and many other cases of undoubted isomorphism, identity of crystalline form is held to indicate an equal

[1] *Handwörterbuch der Chemie*, von Liebig, Poggendorff und Wöhler, 1849, iv. 170, Artikel 'Isomorphismus polymerer,' also in form of a pamphlet entitled 'Isomorphismus und polymerer Isomorphismus,' Braunschweig, 1850, *vide* preface and p. 33. Scheerer has undoubtedly assumed the occurrence of polymeric isomorphism in far too many cases (see Will's *Jahresbericht*, 1865, 192), but the existence of the phenomenon cannot be denied.

[2] *Ann. Chim. Phys.* xiv. 174.

number of atoms, the present atom of potassium must be considered to be composed of at least five actual atoms. It is true that this is possible, but it is by no means probable.

§ 53. A second circumstance which renders the atomic weights deduced from isomorphism uncertain is that each of these conclusions can only be applied to a limited group of elements and compounds. A comparison is therefore only possible within these limits.

It follows from Mitscherlich's researches on the phosphates and arsenates, that phosphorus and arsenic can replace each other in isomorphous compounds in the ratio of 1 to 2·42 parts by weight. Hence it follows that P : As = 1 : 2·42. But the relation which the atomic weight of either of these elements bears to that of oxygen or of hydrogen cannot be determined by isomorphism. The assumption that P = 62 and As = 150 fulfils these requirements just as well as the assumption that P = 31 and As = 75; since 62 : 150 = 31 : 75 = 1 : 2·42.

According to the first view the composition of the anhydrides would be represented by the formulæ PO_5 and AsO_5, according to the latter, by P_2O_5 and As_2O_5. The question has been settled in favour of the latter view by the laws of Avogadro and of Dulong and Petit. Isomorphism could not decide the point. Mitscherlich successively used both formulæ. Similarly the isomorphism which Mitscherlich discovered in a large number of metals such as copper, iron, nickel, cobalt, manganese, zinc, and magnesium can be explained by the old views of Berzelius, according to which the strongly basic oxides of these metals are composed of one atom of metal to two atoms of oxygen (CuO_2,FeO_2,NiO_2, &c.), equally as well as they can by the more recent views in accordance with which these oxides are represented as composed of one atom of metal and one atom of oxygen (CuO,FeO,NiO, &c.)

The isomorphism of the oxides, spinelles, and alums may be just as clearly explained on the assumption that the oxides of aluminium, chromium, and iron are composed according to the old formulæ AlO_3, FeO_3, and CrO_3, as by those at present in use, viz. Al_2O_3, Fe_2O_3, and Cr_2O_3. In either case the replacement is accomplished by equal numbers of atoms. When we remember that, according to Avogadro's law, the atomic

weight of chromium cannot be larger than Cr = 52·4[1] it follows that the formulæ for chromic oxide and chrome iron ore will be Cr_2O_3 and $FeCr_2O_4$ respectively, and it also follows that the formulæ for ferric oxide, alumina, magnetic iron ore, spinelle, &c., will be Fe_2O_3, Al_2O_3, Fe_3O_4, $MgAl_2O_4$, &c.

In almost every group of elements, it is possible to deduce several atomic weights, each of which, nevertheless, may satisfy the laws of isomorphism. It is only when the atomic weight of one of the isomorphous elements has been determined by another method that isomorphism is of use in determining the atomic weights of the other members of the groups.

In many cases a comparison between two groups is rendered possible by one or more elements belonging to several groups. Chromium and manganese are valuable examples of this fact. Mitscherlich discovered that these two metals could not only mutually replace each other, and also a large number of other metals, such as iron, cobalt, nickel, zinc, &c., in many of their isomorphous compounds, but that they could both replace sulphur and selenium, and that manganese could also replace chlorine in their isomorphous compounds. It was the isomorphism of the chromates and manganates with the sulphates and selenates which induced Berzelius to reduce the atomic weights of chromium and manganese to half the values formerly accepted.[2]

This change was at once welcomed. But the isomorphism of the permanganates and perchlorates did not induce chemists to alter the atomic weights of manganese and chlorine in such a way that the isomorphism should appear to be produced by an equal number of atoms.

On the contrary, the composition of potassium permanganate and perchlorate has for many years been represented by several chemists by the formulæ

$$KOMn_2O_7 \text{ and } KOClO_7,$$

whilst, after Mitscherlich's research, Berzelius always expressed their composition thus

$$KOMnO_7 \text{ and } KOClO_7$$
$$\text{or } KOMn_2O_7 \text{ and } KOCl_2O_7.$$

[1] See § 23. [2] Berzelius, *Jahresber.* 1826, 69.

Now that the atomic weight of potassium has again been halved, in order that it may obey Dulong's law, these salts are represented by the formulæ $KMnO_4$ and $KClO_4$, assuming with Berzelius that both the isomorphous salts contain the same number of atoms.

§ 54. In these cases the views of Berzelius have been universally acknowledged, and the atomic weights now used for Cu, Cd, Zn, Ni, Co, Fe, Mn, Cr, S, Se, and Cl agree with Mitscherlich's law of isomorphism, but in other cases the influence of this law led Berzelius to adopt values for the atomic weights which are, according to our present views, entirely incorrect.

After Regnault had confirmed the determination by Dulong and Petit and repeated the demand that the atomic weight of silver should be halved in order that it might follow the law of specific heat, Berzelius[1] declined to accept the proposed change on account of the isomorphism of the silver and sodium compounds. When Regnault afterwards succeeded in determining the specific heat of sodium this objection proved to be illusory, since the atomic weight of sodium had also to be halved in order that it might follow the laws of Dulong and Petit.

The supposed isomorphism of garnet and magnetic iron ore led Berzelius to fix the atomic weight of silicon in such a way that anhydrous silicic acid was represented by the formula SiO_3,[2] whereas, according to Avogadro's law and the real isomorphism of the compounds of silicon with those of tin, titanium, and zirconium, the atomic weight of silicon can only be two-thirds of the value accepted by Berzelius, and the formula of the anhydrous acid SiO_2.

As Berzelius occasionally made mistakes in his deductions from isomorphism, it is not surprising that other chemists have also arrived at erroneous conclusions. Such conclusions have been the more frequently made in those cases in which similar crystalline form had not been shown to be due to a similarity in the number and arrangement of the atoms.

According to Mitscherlich[3] barium permanganate has the

[1] *Lehrb.* 5. Aufl. iii. 1215. [2] *Ibid.* iii. 1204, and *loc. cit.*
[3] *Pogg. Ann.* 1832, xxv. 301.

same crystalline form as anhydrous sodium sulphate and selenate.

The composition of these three salts is at present expressed by the formulæ

$$BaMn_2O_8,\ Na_2SO_4,\ \text{and}\ Na_2SeO_4,$$

which do not contain an equal number of atoms. In order to attain this uniformity, Clarke[1] has proposed to double the atomic weight of sodium (*i.e.* = four times the present value) and use the formulæ

$$BaMn_2O_8,\ NaS_2O_8,\ \text{and}\ NaSe_2O_8.$$

The crystalline form of these compounds is at the present time the sole ground for the proposed alteration of the atomic weights. Whether the identity of crystalline form has its origin in a hitherto undiscovered similarity in the arrangement of the atoms, or is merely due to chance, cannot be decided at present.

These and numerous similar cases impart an element of uncertainty to the atomic weights deduced from isomorphism alone. This is especially the case since Marignac called attention to the fact that equality in the number of atoms in a molecule is not absolutely necessary in isomorphous compounds.[2]

He considers it a necessary assumption that if two compound bodies contain the same elements or group of elements as the preponderating common constituent, they are to be regarded as isomorphous only when the other elements, to whose presence the difference of composition is due, do not belong to a similar or isomorphous group of elements.

Marignac has moreover shown that certain groups of atoms can replace each other in isomorphous compounds even when the individual atoms forming these groups do not usually exhibit isomorphism. One of the most striking examples of this kind is the isomorphism of titanium fluoride with the oxy-fluorides of niobium and tungsten. Marignac's

[1] *Lieb. Ann.* 1838, xxvii. 167; Kopp, *ibid.* 1840, xxxvi. 4.
[2] *Lieb. Ann.* 1864, cxxxii. 29.

research [1] shows that the following compounds are isomorphous:

K_2TiF_6,H_2O, K_2NbOF_5,H_2O, and $K_2WO_2F_4,H_2O$,

also

$CuTiF_6$, $4H_2O$, $CuNbOF_5$, $4H_2O$, and $CuWO_2F_4$, $4H_2O$.

In these isomorphous compounds the mutually replaceable groups are TiF_2, NbOF, and WO_2; but isomorphism between their individual constituents has not been observed. The isomorphous replacement of Ti by Nb and W, or of F by O, is unknown. Of course it is possible that such an occurrence may be observed at some future period, although it is not probable, since O is generally replaced by F_2 and not by F in chemical decompositions, and in most other cases O is equivalent to F_2 and not to F.

§ 55. This extension of Mitscherlich's law of isomorphism has rendered its application to the determination of atomic weights much less trustworthy. It must only be used with great caution in most cases. Nevertheless isomorphism still retains a position of great importance in atomic weight determinations, but the form in which its influence is exerted has undergone a material change. In the time of Berzelius it was decisive, but now it chiefly serves, on the one hand, the purpose of detecting doubtful and incorrect determinations of the atomic weights and of causing their redetermination by the laws of Avogadro and of Dulong and Petit, and, on the other hand, it is used for confirming the accuracy of the atomic weights which have been determined by these methods. Numerous observations have clearly proved that the values for the atomic weights of the elements deduced from the vapour densities of compounds or from the specific heats of the elements, obey the law of isomorphism as well, and frequently better, than any values for the atomic weights founded on other standpoints, such as the chemical or electrolytical equivalents.

A large number of cases are known in which, when atomic weights were used which did not obey the laws of Avogadro and of Dulong and Petit, the identity of crystalline form observed in certain compounds could not formerly be ascribed

[1] *Compt. Rend.* Jan. 30, 1865, lx. 234; Will's *Jahresbericht*, 1865, 198.

to a similarity in the arrangement and number of atoms. The similarity in constitution at once becomes apparent on the introduction of the atomic weights at present in use.

Amongst the most striking examples of this kind is the isomorphism of chili saltpetre with calc spar, and of nitre with arragonite. The similarity of crystalline form appeared to be purely accidental so long as the composition of these bodies was represented by Gmelin's equivalent weights :

$$NaO.NO_5 = NaNO_6 \text{ and } CaO.CO_2 = CaCO_3$$
$$KONO_5 = KNO_6 \text{ and } CaO.CO_2 = CaCO_3.$$

But the formulæ now in use show that the similarity of crystalline form depends on the equal number of atoms contained in the molecules: [1]

$$NaNO_3 \text{ and } CaCO_3,\ KNO_3 \text{ and } CaCO_3.$$

The same crystalline form also occurs in the red silver ores, Ag_3AsS_3 and Ag_3SbS_3, which do not contain the same number of atoms as the preceding compounds.

§ 56. An undoubted instance of identity of crystalline form without the corresponding analogous composition demands that the former analytical investigations should be submitted to further proof.

The isomorphism of Rose's so-called 'Unterniob' fluoride with the corresponding fluorides of titanium and tin led Marignac to the conclusion that Rose's so-called 'Unterniob' could not be an element or an allotropic form of niobium, but that in all probability its supposed atomic weight, which can replace TiF and SnF in isomorphous compounds, must be composed of an atom of a metallic and an atom of a non-metallic element. Closer investigation proved this to be the fact, and showed that 'Unterniob' is composed of an atom of niobium and an atom of oxygen. The group NbO is therefore isomorphous with TiF and SnF, in accordance with Mitscherlich's law.[2] Marignac's determination of the atomic weight of niobium (Nb = 94 when H = 1) has been confirmed by the

[1] Schaffgotsch, *Pogg. Ann.* 1839, xlviii. 335; H. Kopp, *Lieb. Ann.* 1863, cxxv. 372; Marx, Frankenheim, and Sénarmont (*Compt. Rend.* 1854, xxxviii. 105) first pointed out that these are cases of real isomorphism. See also *Ber. d. deut. chem. Ges.* 1871, 53 and 104; also H. Kopp, *ibid.* 1879, 914.

[2] *Compt. Rend.* 1865, lx. 234.; *Lieb. Ann.* 1865, cxxxv. 49.

vapour density determination of the chloride $NbCl_5$ by Deville and Troost.[1]

The isomorphism of vanadinite with apatite, pyromorphite, and mimetisite, which formerly could not be regarded as having an analogous composition, induced Roscoe to investigate the compounds of vanadium afresh and to redetermine its atomic weight. He found that what had formerly been regarded as an atom of vanadium really consisted of two atoms of vanadium and two atoms of oxygen.[2] He confirmed this result by Avogadro's law by determining the vapour density of the oxychloride $VOCl_3$[3] and of the chloride VCl_4.[4]

After the alteration in the atomic weight, these isomorphous compounds exhibit analogous composition:

$Pb_5V_3O_{12}Cl$ $\qquad$ $Ca_5P_3O_{12}F$ $\qquad$ $Ca_5P_3O_{12}Cl$

Vanadinite $\qquad$ Apatite

$Pb_5P_3O_{12}Cl$ $\qquad$ $Pb_5As_3O_{12}\,Cl$

Pyromorphite $\qquad$ Mimetisite

Although the results deduced from the law of isomorphism appear most convincing, both in these and many other cases, it is at the present time always considered necessary to confirm the atomic weights obtained by this method either by a determination of the atomic heat or of the molecular volume of one or more compounds of the particular element. The atomic weight is not regarded as definitely fixed until it has received this confirmation.

The atomic weight of an element can only be determined with certainty by the law of isomorphism, when the element forms numerous compounds which have been carefully and accurately analysed and which exhibit indisputable isomorphism with compounds of another element the atomic weight of which has been definitely fixed by Avogadro's law or by the law of Dulong and Petit. Since Marignac's research[5] on the isomorphous compounds of tantalum and niobium, the atomic weight of tantalum has been taken as Ta = 182, correspond-

[1] *Compt. Rend.* 1865, lx. 1221; *Lieb. Ann.* 1865, cxxxvi. 249.
[2] *Lond. Phil. Trans.* 1868, 1; *Lieb. Ann.* 1868; Suppl. vi. 77.
[3] *Lieb. Ann.* 1868; Suppl. vi. 108. [4] *Ibid.* 1870; Suppl. vii. 75.
[5] Will's *Jahresber.* 1866, 200.

ing to that of niobium Nb = 94, although the specific heat of tantalum is unknown and the vapour density determinations of tantalum chloride by Deville and Troost,[1] made with impure material, do not correspond with that value for the atomic weight.

Conclusions of this kind must be made with great caution. The supposed isomorphism between the sulphates of didymium and cadmium led to the adoption of a value for the atomic weight of the former element which is only two-thirds of the value deduced from the specific heat observations. But H. Kopp[2] has recently pointed out that this is not in reality a case of isomorphism, since the salts do not crystallise together.

Although in the present state of our knowledge isomorphism alone is not as a rule sufficient for fixing the atomic weight, it is nevertheless a very important means of testing and confirming the atomic weights which have been deduced from the vapour density or specific heat determinations. In this way it has done much to lead to their general adoption.

The values determined for the atomic weights by the laws of Avogadro and Dulong and Petit agree so much better with the laws of isomorphism than with any other values which have ever been used, that these laws only attained their full import after the introduction of the new atomic weights. Many important advances in our knowledge of this law may now be expected which were impossible so long as generally acknowledged principles for the determination of the atomic weight were wanting.

In the immediate future, at all events, the law of isomorphism will have more to gain from the present methods of atomic weight determination than the latter from the law of isomorphism.

[1] Will's *Jahresber.* 1866, 203.
[2] *Ber. d. deut. chem. Ges.* 1879, 909.

V.

THE NATURE OF CHEMICAL ATOMS.

§ 57. Although the knowledge of the atomic or equivalent weights was indispensable to chemists in their analytical and stochiometrical researches, the peculiar nature of the atoms rarely formed the subject of their investigations. Chemists have seldom attempted to answer or discuss the question of the nature of the atoms; they have generally overlooked or avoided it. Very little is known with any degree of certainty concerning the nature of the atoms, but it is to be hoped that the beginning which has actually been made may eventually lead to a hypothesis on the nature of the atoms capable of accurately explaining the results of experimental observation.

It has already been mentioned in § 3 that the atoms are beyond the field of direct observation and are purely hypothetical. But the atomic hypothesis has aquired a high degree of probability since a theoretical explanation of a large number of chemical and physical phenomena can only be given with its aid.

But if the assumption of individual isolated particles of matter possessing definite and unvarying weights forms the indispensable foundation of every chemical theory and of almost every physical theory, there is still room for speculation concerning the properties of these elementary particles of matter or atoms.

It is not disputed that the atoms must of necessity possess weight, but for a long time it was believed that it would only be possible to measure their relative and not their absolute weight. Recently an approximate measurement of the absolute weight of the molecules, and therefore also of the atoms, has been made, based upon measurements of the space

occupied by these smallest particles. The question of th space they occupy has been frequently discussed. Dalton the founder of our chemical atomic theory, definitely ascribe to his atoms dimensions, just as the representatives theoretical physics in the seventeenth and first half of th eighteenth century generally assumed the existence of ver minute particles of matter as the basis of their speculation and hypotheses.

In more recent times the idea is occasionally expresse more or less distinctly that the atoms are infinitely small, it is expressly stated that they do not occupy space, but ar mere centres of force, *i.e.* points round which forces or move ments are directed. This idea has lost all support in con sequence of the new investigations in the different fields molecular physics, which have shown that the molecules a least must have dimensions, since the assumption of infinitel small particles leads to results which do not agree wit observed facts.

The theoretical investigation of the most varied effects molecular action has rendered it possible to arrive at a approximate valuation of the limits within which the dimen sions of the molecules of different bodies must lie. Some tim ago Sir William Thomson collated these results [2] in a popula lecture, and showed that the conclusions arrived at from per fectly distinct investigations exhibited a wonderful amount agreement which strongly increased the probability of thei correctness.

These results show that the diameter of a molecule of an substance can never be smaller than the fifty-millionth par of a millimetre, but is often considerably larger. The be haviour and properties of gases and vapours furnish differen means for determining the size of their molecules. Th comparison of their volumes in the liquid and gaseou state, their deviations from Boyle's and Marriotte's law, an their frictional constants, permit in the first place of th determination of the volume occupied by all the particle

[1] Dalton's *New System of Chemical Philosophy.*

[2] *Nature*, March 31, 1870; *Amer. Journ. of Science and Arts*, [2] l. 38 *Lieb. Ann.* 1871, clvii. 54.

contained in a given volume. The volume occupied by an individual particle can next be ascertained, then the number of particles, and finally the weight of an individual particle can be approximately calculated.[1]

In this way it is shown that the diameter of a molecule of those substances which have been sufficiently investigated is generally smaller than one-millionth of a millimetre, but is larger than the ten-millionth. Under a pressure of one atmosphere and at the mean temperature of *circa* 20°, 1 cubic millimetre of any gaseous substance which obeys Avogadro's law contains about 21 trillions of molecules. But as one c.c. of hydrogen under the given conditions weighs 0·0835 milligramme, the weight of a molecule of hydrogen must be $\mathfrak{H} = H_2 = \frac{0{\cdot}0835}{21{\cdot}10^{18}} = \frac{4}{10^{21}} = 0{\cdot}000{,}000{,}000{,}000{,}000{,}004$ mgrm., or a quadrillion molecules of hydrogen weigh about four grammes. From these data the absolute molecular weight of any other substance which obeys Avogadro's law can easily be calculated.

§ 58. The weight and volume of the atoms cannot be directly determined from the weight of the molecules, as, in the first place, the absolute number of atoms forming the molecules is not known, and, secondly, it is not known whether the space taken up by the molecule is completely filled with atoms or whether the atoms are separated from each other by intervening spaces.

In the remarks on the determination of molecular weights (§ 3) the number of atoms united to form a molecule was, indeed, determined, but with (§ 22) the reservation that the actual atomic weight might possibly be a simple fraction of the value obtained, in which case the number of atoms in a molecule would be a multiple of the number found according to Avogadro's law. But if it cannot be proved with absolute certainty that a molecule of hydrochloric acid does, as we assume, really contain one atom of hydrogen and one atom of chlorine and not two or three atoms of each element,

[1] For details see O. E. Meyer's *Kinetische Theorie der Gase*, Abschnitt iii., 'Ueber die unmittelbaren Eigenschaften der Molekeln,' especially paragraphs 101-107.

it may, however, be assumed that a molecule of hydrochloric acid does not contain fifty or a hundred simple atoms.

If it contained, for example, fifty atoms of hydrogen and fifty atoms of chlorine, it would be possible for one or more atoms to be removed from this number without destroying the equilibrium of the whole system. But if a single atom of chlorine was missing it would lower the proportion by weight of the two constituents from 1 : 35·47 to 1 : 34·69, an alteration which would lie beyond the limit of error of a quantitative estimation.

In an extensive research on the atomic weights of the elements, Stas[1] has submitted the question whether the relation between the chemical constituents in compounds is constant or variable, to a special proof.

The experimental determinations were carried out with the extraordinary accuracy peculiar to Stas, so that very small fluctuations in the atomic weights of the elements would have been detected if they ever occurred. For example, in the experiments for ascertaining the ratio of the atomic weights of iodine and silver in the iodide and in the iodate, a variation of one hundred-thousandth part of the value of one of these numbers could not have escaped detection.[2]

Since no variation was observed, it was concluded that that proportion does not vary one hundred-thousandth of its value, and it is probably absolutely constant. This constant proportion in which both substances unite would scarcely occur if the number of combining atoms was large.

It may therefore be assumed that the number of atoms united to form a molecule is not very large, and that the size of the atom in proportion to the size of the molecules is not excessively small. But the experiments of Kundt and Warburg, mentioned in § 27, make it highly probable that the molecular weight of mercury is actually equal to the atomic weight itself, and not a multiple of it ; for this element, at least, the atomic weight determined according to Avogadro's law and that of Dulong and Petit, forms only one single homogeneous particle of matter. It is highly probable, indeed

[1] J. S. Stas, *Nouvelles Recherches sur les Proportions Chimiques*, &c. 1. mémoire, 27–108.

[2] *Ibid.* pp. 68–77.

almost certain, that the same holds true for all other atomic weights determined by these laws.

The number of atoms contained in a molecule can therefore be regarded as identical with the conclusions drawn from Avogadro's law. But it does not follow that the space occupied by the molecule is equal to the sum of the spaces occupied by the atoms. Since the atoms are in a state of active motion, it is almost certain that the space occupied by the molecule is not completely filled by the atoms; but, on the other hand, it is not probable that the space which the atoms really occupy is very small in proportion to the space taken up by the molecule. It may therefore be concluded that, although the space occupied by an atom is very small, it is not infinitely small.

§ 59. Whether the atoms really are *ἄτομοι*, *i.e.* absolutely indivisible particles of matter, whether they are the ultimate elements into which matter can be decomposed, is a question closely connected with that of the space occupied by the atoms. This problem has not yet been definitely settled, but there are many reasons for believing that, although the atoms are particles of a lower rank than the molecules, they are not the ultimate smallest particles of matter. It is probable that just as those masses which perceptibly occupy space are composed of molecules, and molecules or particles of the first order are composed of atoms or particles of the second order, so atoms are composed of particles of matter of a third and simpler order. This view is supported by the reflection that if atoms are unchangeable and indivisible, just as many elementary forms of matter must exist as there are chemical elements. The existence of some sixty or more entirely different forms of primordial matter is improbable; the knowledge of certain properties of the atoms, especially the relations exhibited by the atomic weights of different elements, rendering this all the more unlikely. Soon after Dalton's atomic theory had met with general recognition, Prout,[1] in 1815, brought forward the view that the primordial matter of which all elements are composed is hydrogen, and consequently the atomic weights of all the other elements are simple multiples

[1] *Annals of Philosophy*, by Th. Thomson, vi. 321.

of the atomic weight of this primal element. This view, which was supported by Th. Thomson, and afterwards by Dumas, is however not in agreement with the most exact quantitative determinations. The investigations of Turner, Berzelius, Marignac, and Stas have shown that the atomic weights of many of the elements are nearly, but not exactly, simple multiples of the atomic weight of hydrogen, and cannot therefore be expressed by whole numbers when the atomic weight of hydrogen is taken as the unit, nor do they bear a simple relation to one another.[1]

It is however very remarkable, as Marignac has pointed out, that a large majority of the atomic weights are almost exact multiples of the atomic weight of hydrogen. This can hardly be purely accidental. It is possible that the atoms of all or many of the elements chiefly consist of smaller particles of matter of one distinct primordial form, perhaps hydrogen, and that the weights of the atoms do not bear a simple relation to one another because the atoms contain, in addition to the particles of this primordial matter, varying quantities of the matter which fills space and is known as the luminiferous ether, which is perhaps not quite devoid of weight. This appears to be the only permissible hypothesis. Its extension may prove of service to the science in the future, although this can hardly be expected at present, as its accuracy has neither been proved nor disproved.

§ 60. The investigation of the nature and possible composition of atoms must first of all be directed towards increasing by further researches the material for speculation. It must then be submitted to criticism, correctly and systematically arranged. In this direction a promising beginning has already been made. The tolerably exact atomic weight determinations which Berzelius made of almost all the known elements have

[1] For the history of Prout's hypothesis see H. Kopp, *Geschichte der Chemie*, ii. 391; J. J. Berzelius, *Lehrbuch d. Chemie*, 5. Aufl. iii. 1173; J. S. Stas, *Recherches sur les Rapports Réciproques des Poids Atomiques*, Bruxelles, 1860, pp. 6 and 131 (*Bull. Acad. Roy. Brux.* [2] x. No. 8); *Nouvelles Recherches sur les Lois des Proportions Chimiques*, &c. 1865, Introduction. (*Mém. Acad. Roy. Bruxelles*, xxxv. 1865); also *Lieb. Ann.* Suppl.-Bd. iv. 168; C. Marignac, *Arch. Sciences Phys. Nat.* 1860, ix. 101; 1865, xxiv. 375; also *Lieb. Ann.* Suppl.-Bd. iv. 201.

been carefully corrected and replaced by more accurate values. In the fourth decennium of the present century C. Marignac attained an extraordinary degree of accuracy and certainty in his systematic and comprehensive quantitative determinations, and more recently Stas has perfected the methods of determining atomic weights to such an extent that the values for the atomic weights of a whole series of elements have been determined to the thousandth, and in some cases to the ten-thousandth part of their value.[1] This result appears the more valuable when it is remembered that the atomic weights of many of the elements which have not yet been investigated by such excellent methods obviously contain errors, often to the extent of the hundredth and even the tenth of their value.[2]

It will only be possible to determine exactly the mutual relation between the atomic weights of the different elements, to discover their original import, and to gain in this way a deeper insight into the nature of the atoms, when the atomic weights of all or most of the elements have been determined with some degree of accuracy.

Although at present the determinations of these relations are, as a rule, merely approximate, and are deficient in accuracy, nevertheless they deserve the most careful attention, as the starting-point of investigations in this uncultivated field of research. It has long been noticed that the values of the atomic weights of allied elements bear a certain relation to each other. Thus many similar elements have almost identical atomic weights. In many groups consisting of three closely allied elements, called triads by Döbereiner,[3] the atomic weight of one of these is nearly the arithmetical mean of the other two.

Since Leopold Gmelin in 1826 called attention in his treatise[4] to relations of this description the subject has been frequently discussed by different chemists, more particularly

[1] See previous note.

[2] *Vide Die Atomgewichte der Elemente aus der Original-Zahlen neu berechnet*, von L. Meyer und K. Seubert, p. 240. Leipzig, 1883.

[3] *Pogg. Ann.* 1829, xv. 301.

[4] 3rd edition, 1826, . 35; 4th edition, 1842, i. 52; 5th edition, 1852, i. 47.

by Max Pettenkofer, J. J. Dumas, P. Kremers, J. H. Gla stone, J. P. Cooke, Low, W. Odling, E. Lenssen, J. Merc M. C. Lea, J. A. R. Newlands, Carnelley, Crookes, and other The question also of the compound nature of the atoms h been frequently discussed. In fact, this view becomes e tremely probable, since the atomic weights of certain groups closely related elements exhibit relations to each other simi to those found to exist between the molecular weights certain series of analogous organic compounds.

For example:

Atoms.		Molecules.		Radicles.	
Li	= 7·01	Methyl alcohol, CH_4O	= 31·93	Methyl = CH_3	= 14·97
Diff.	15·98	CH_2	= 13·97	CH_2	= 13·97
Na	= 22·99	Ethyl alcohol, C_2H_6O	= 45·90	Ethyl = C_2H_5	= 28·94
Diff.	16·04	CH_2	= 13·97	CH_2	= 13·97
K	= 39·03	Propyl alcohol, C_3H_8O	= 59·87	Propyl = C_3H_7	= 42·91

It may be easily assumed that the difference of the atom weights of these metals depends on a difference in the comp sition of their so-called atoms, as is shown above to be the ca in the analogous organic compounds or radicles. In this ca the atoms will not be indivisible values, but compounds particles of a simpler order, *i.e.* compound radicles.

The analogy in their behaviour with that of the ackno ledged compound radicles could be easily explained on th hypothesis.

There are numerous cases of similar relations between t atomic weights. But the various authors who have work on this subject have represented these relations in differe ways, especially was this the case before a uniform rule h been established for determining atomic weights, and wh equivalent and atomic weights were frequently confuse Numerical relations were sought for where they did not exi and, what was much more dangerous, the values obtained experiment were frequently altered in order that they mig exhibit relations not warranted by direct observation.

Since most investigators believed in Prout's hypothes

[1] The literature of the subject is given in the *Jahresberichte über d. Fo schr. d. Chemie*, von Liebig u. Kopp, Kopp u. Will, Will, 1851, 291, 292; 18 294: 1853, 312; 1854, 284, 285; 1857, 27-36; 1858, 13, 14; 1859, 1-7; 18 5; 1862, 7; 1863, 13; 1864, 16; 1865, 17.

and therefore converted the atomic weights obtained empirically into the nearest whole number, they naturally obtained as the difference of two atomic weights, whole numbers, which were frequently multiples of 8 or 8 itself.

The formula generally used for representing these relations was $A = a + n.8$, in which A = the atomic weight and a and n small whole numbers. It has not yet been proved, and it is, indeed, very improbable, that the exact values of the atomic weights can be represented by formulæ of this description.

§ 61. It was only after Cannizzaro[1] had explained the supposed contradiction between the law of Avogadro and that of Dulong and Petit by pointing out that the former determined the molecular and the latter the atomic weight, and after he had attributed to both rules the signification which is now generally received (see §§ 2 and 3), that the relations between the values of the atomic weights acquired a greater uniformity, and permitted a systematic tabulation[2] of all the elements the atomic weights of which were known.

This system is based on the notion that the properties and characters of the elements are determined by the magnitude of their atomic weights, or, to express it mathematically, the properties are functions of the atomic weights.

If the atoms are arranged in a simple series, merely in the order of their atomic weights, ranging from the lowest upwards, their properties change from member to member, but recur to a greater or lesser extent for certain differences in the value of the atomic weights. No analogue of hydrogen, the first member of the series, is known. But the characteristic properties of the second member, lithium (Li = 7·01), recur after an increase of 16 units in the atomic weight in the ninth member, sodium (Na = 22·99), and again after a similar increase in the fifteenth member, potassium (K = 39·03).

Roughly speaking, there is a difference of 46 units between the atomic weight of potassium and the fourth alkali metal, rubidium (Rb = 85·2), and again a difference of 47 units between the atomic weight of the latter and that of caesium (Cs = 132·7). In this series of atomic weights a metal of the

[1] Paragraph xviii. 43, and xxxiv. 79, *loc. cit.*

[2] For the history of this subject see *Ber. d. deut. chem. Ges.* 1880, 259.

alkaline earths is associated with each of the alkali metals, *e.g.* beryllium (Be = 9·1)[1] with lithium, magnesium (Mg = 23·94) with sodium, calcium (Ca = 39·9) with potassium, strontium (Sr = 87·2) with rubidium, and finally barium (Ba = 136·9) with caesium. The atomic weights of the two groups exhibit almost the same differences. In the same way the metals of the alkaline earths are followed by other elements which also resemble each other and exhibit similar differences in their atomic weights.

If the series is interrupted at corresponding points, that is, at elements of a similar nature, several shorter series of analogous construction are formed, which may be so arranged that the elements follow each other in the order of their atomic weights in the horizontal rows, whilst the vertical rows are composed of members of the natural families.

The first member of each horizontal row is directly connected with the last member of the previous one. The rows from left to right in the following table contain the elements (with the exception of H) the atomic weights of which have been accurately determined,[1] arranged in the order of their atomic weights in such a way that the first member of each horizontal row is directly connected with the last member of the previous row. If this table is rolled round an upright cylinder so that the right side touches the left, then Ni will be in contact with Cu, Pd with Ag, and Pt with Au. In this way a continuous series of all the elements in the order of their atomic weights is easily obtained arranged in a spiral form.[2] The elements occurring in the same vertical column form a natural family, but the members of the group are not all equally closely

[1] The great difficulty of separating and purifying the recently discovered earthy metals renders it probable that many of them will, like philippium, be proved not to exist (*vide* Roscoe, *Chem. Soc. Jour.* 1882, 277); they have therefore been omitted from this table.

[2] Instead of this simple spiral arrangement of the elements, which, when placed round a cylinder, is a suitable means of illustrating this relationship, H. Baumhauer has published another plan arranged on a flat surface (*Die Beziehungen zwischen dem Atomgewichte und der Natur der chemischen Elemente*, Braunschweig, 1879), which, however, is too arbitrary to represent an impartial expression of the facts. The graphic representation of the atomic weights by P. Kremers (*Physicalisch-chemische Untersuchungen*, Wiesbaden, 1869–70) is still more artificial and difficult to understand.

related. In most groups of eight or nine members, four or five of the elements are more intimately connected together than the remaining three or four, which however again closely resemble each other. The five alkali metals, Li, Na, K, Rb, and Cs in the first column bear a close resemblance to each other, whilst the three heavy metals, Cu, Ag, and Au, which possess similar properties in many respects, only resemble the former metals in certain points, namely, in the isomorphism of many of their compounds, and in their power of replacing a single atom of hydrogen in forming salts. Similarly the second column contains two groups, viz. the alkaline earths, Be, Mg, Ca, Sr, Ba, and the heavy metals, Zn, Cd, Hg, which only possess a few properties in common, namely, their divalence and the isomorphism of many of their compounds. And in the same way each of the remaining columns contains two distinct groups, which are, however, connected to a certain extent.

In order to bring about a regular system some spaces must be left vacant in the accompanying table, and some elements whose atomic weights have been found to be nearly equal, and cannot be regarded as having been accurately determined, have been arranged in a somewhat different order from that of their generally received atomic weight, viz. tellurium before iodine, osmium before iridium, platinum, and gold. The reasons for this rearrangement will be discussed in §§ 81, 82.

§ 62. An examination of each horizontal row in the table exhibits the changes in the properties of the elements. The changes are sometimes abrupt and sometimes gradual. On closer inspection the rules and laws which govern the change of the chemical and physical properties are clearly perceptible. Almost all the properties of the elements are closely connected with the atomic weights; they are periodic functions of the values of the atomic weights. One of the few properties which has been accurately determined in the case of most of the elements is the density in the solid state; and this property clearly shows itself to be a periodic function of the atomic weight, since it increases and decreases regularly with an increase in the atomic weights. This connection is most conspicuous if we compare the ratio between the atomic weights

I.	II.	III.	IV.	V.	VI.	VII.	VIII.		
Li 7·01	Be 9·08	B 10·9	C 11·97	N 14·01	O 15·96	F 19·06			
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			
Na 22·99	Mg 23·94	Al 27·04	Si[1] 28	P 30·96	S 32·08	Cl 35·37			
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			
K 39·03	Ca 39·91	Sc 43·97	Ti 48	V 51·2	Cr 52·45	Mn 54·8	Fe 55·88	Co 58·6	Ni 58·6
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			
Cu 63·18	Zn 64·88	Ga 69·9	? U 72	As 74·9	Se 78·87	Br 79·76			
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			
Rb 85·2	Sr 87·3	? Y 89·6	Zr 90·4	Nb 93·7	Mo 95·9	? 99	Ru 103·5	Rh 104·1	Pd 106·2
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			
Ag 107·66	Cd 111·7	In 113·4	Sn 117·35	Sb 119·6	Te 126·3	I 126·54			
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			
Cs 132·7	Ba 136·86	La 138·5	Ce 141·2	Di[2] 145	? 151	? 152	Os 195 ?	Ir 192·5	Pt 194·3
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			
? 165	? 170	Yb 172·6	? 176	Ta 182	W 183·6	? 185			
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			
Au[3] 196·2	Hg 199·8	Tl 203·7	Pb 206·39	Bi 207·5	? 210	? 211			
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			
? 222	? 226	? 230	? Th 231·96	? 234	? U 239·8				

[1] Thorpe and Young (*Chem. Soc. Journ.* 1887) find the atomic weight of silicon to be 28·83. [2] *Vide* note 7, p. 123. [3] *Vide* note 4, p. 161.

ıd the densities, instead of the densities themselves; in ;her words, if we consider the volume occupied by the atomic eight instead of the weight contained in the unit of volume.

At present this space, which is known as the atomic olume, cannot be measured absolutely, but a relative measure- ıent may be made by taking such quantities of the different lements as are proportional to their atomic weights, and omparing the space occupied by these quantities. If, as sual, the density of water is taken as unit and the space ccupied by the unit weight of water be the unit of volume, hen the values of the atomic volumes are represented by the uotient of the atomic weight by the density of the given lement. The atomic weight of lithium =7·01, the density f the metal compared with water is 0·59; the atomic volume s therefore $V = \frac{7 \cdot 01}{0 \cdot 59} = 11 \cdot 9$; or, expressed in the metric ystem of weights and measures, 7·01 grammes of lithium ccupy a space of 11·9 cubic centimetres.

If the atomic volumes of all those elements the atomic eights of which have been determined, and of which the nsities in the solid state are known, are calculated by a nilar method by comparing these volumes, many regulari- s are at once evident. Similar elements frequently have ıal, or nearly equal, atomic volumes. Thus, for example, atomic volumes of Cl, Br, and I are nearly equal, = 26 approximately; V = 7 for Mn, Fe, Co, and Ni; for Rh, Pd, Os, Ir, Pt, V = 9; for Ag and Au, V = 10. In er groups, V increases with the atomic weight. Thus, for mple, in the phosphorus and sulphur families

?) = 13·5; V (As) = 13·2; V (Sb) = 17·9; V (Bi) = 21·1.
5) = 15·7; V (Se) = 17·1; V (Te) = 20·2.

This increase, with an increase in atomic weight, is very ked in the group of the alkali metals; *e.g.*

.i) = 11·9; V (Na) = 23·7; V (K) = 45·4; V (Rb) = 56·1; V (Cs) = 70·6.

These numbers are in the ratio 1 : 2 : 4 : 5 : 6.

These very different relations do not appear to be in any

way connected with each other until the relation between atomic volume and atomic weight is regarded from a common standpoint, when the atomic volume is seen to be a function of the atomic weight.[1]

A remarkable periodicity is exhibited in the changes which the atomic volume undergoes with increasing atomic weight. In a series of the elements arranged according to their atomic weights, the atomic volume periodically increases and decreases. Its maxima occur with the alkali metals Li, Na, K, Rb, and Cs; the minima occur with those elements the atomic weights of which lie midway between two alkali metals.

The table on the next page contains the elements arranged in the order of their atomic weights, as in the table in § 61. The horizontal rows are so broken up that the elements having the maximum atomic volumes are found in the first row. The less known metals of the earths are omitted.

Under the atomic symbol of each element its density in the solid state, D, compared with water as unity is given, and under this the quotient of its atomic weight by its density, viz. its atomic volume. It is easily seen that both these values periodically increase and decrease; the first two horizontal rows contain a whole period in which the density passes through the maximum from one minimum to another. After the third row, each period embraces two rows, the density increases and the atomic volume diminishes in the first, whilst in the following columns the reverse obtains.

Possibly another row ought to be inserted after that beginning with Cs. It would, if the atomic weight has been correctly determined, contain erbium and other earthy metals.

§ 63. The relation between the atomic volume and atomic weight is still more clearly depicted by the graphic representation contained in the article by the author, which has been previously mentioned.

In fig. 1 of the table found at the end of this book, the elements are arranged on the horizontal axis of the abscissæ,

[1] Lothar Meyer, 'The Nature of the Chemical Elements as Functions of their Atomic Weights,' *Lieb. Ann.* 1870; Suppl.-Bd. vii. 354.

RELATION BETWEEN ATOMIC WEIGHT AND ATOMIC VOLUME.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.		
D	Li 0·59	Be 1·64	B [1] 2·68	C [2] 3·3	N ?	O ?	F ?			
V	11·9	5·6	4·0	3·6	?	?	?			
D	Na 0·97	Mg 1·74	Al 2·56	Si 2·49	P [3] 2·3	S [4] 2·04	Cl [5] 1·38			
V	23·7	13·8	10·6	11·2	13·5	15·7	25·6			
D	K 0·86	Ca 1·57	Sc ?	Ti ?	V 5·5	Cr 6·8	Mn 8·0	Fe 7·8	Co 8·5	Ni 8·8
V	45·4	25·4	?	?	9·3	7·7	6·9	7·2	6·9	6·7
D	Cu 8·8	Zn 7·15	Ga 5·96	—	As 5·67	Se 4·6	Br [6] 2·97			
V	7·2	9·1	11·7		13·2	17·1	26·9			
D	Rb 1·52	Sr 2·50	? Y ?	Zr 4·15	Nb [8] 6·27	Mo 8·6	—	Ru 12·26	Rh 12·1	Pd 11·5
V	56·1	34·9	?	21·7	15·0	11·1		8·4	8·6	9·2
D	Ag 10·5	Cd 8·65	In 7·42	Sn 7·29	Sb 6·7	Te 6·25	I 4·94			
V	10·2	12·9	15·3	16·1	17·9	20·2	25·6			
D	Cs 1·88	Ba 3·75	La 6·2	Ce 6·7	Di [7] 6·5					
V	70·6	36·5	22·3	21·0	22·3					
D			? Yb ?	—	Ta [8] 10·8	W 19·13	—	Os 22·48	Ir 22·42	Pt 21·50
V			?		16·9	9·6		8·7 [9]	8·6	9·1
D	Au 19·3	Hg 13·59	Tl 11·86	Pb 11·38	Bi 9·82					
V	10·2	14·7	18·1	18·1	21·1					
D				Th 11·1		U 18·69				
V				20·9		12·8				

at distances from zero proportional to their atomic weights. The position of each element is denoted by the corresponding atomic symbol, and from each of these points an ordinate is

[1] Not pure. See Hampe, *Lieb. Ann.* 1876, clxxxiii. 75.
[2] Diamond: for graphite, D = 2·15, V = 5·58.
[3] Black, crystalline.
[4] Rhombic crystalline.
[5] Density of liquid chlorine.
[6] Density of liquid bromine at 4°.
[7] According to recent researches, the didymium would probably be impure.
[8] H. Rose determined the density of niobium and tantalum from impure material. D is probably too low and V too high.
[9] Probably only 8·5 if Os = 192.

drawn which is proportionate in length to the atomic volume of the given element. A curve uniting the extremities of these ordinates represents the variations which the atomic volumes undergo for increasing atomic weights. But since the density, and consequently the atomic volume, of a large number of elements is not known, these curves cannot be completed. The gaps in the table are, however, partly filled up by dotted lines on the assumption, which is apparently justified by the complete course of the curves, that the curve is analogous for analogous elements, *e.g.* the curve from C through N, O, F to Na resembles the curve from Si through P, S, Cl to K; further, the curve from Ca to V resembles that from Sr to Nb, &c. On these hypothetically completed curves the symbols of the elements are printed in written characters (*C, N, O, J*, &c.), elsewhere in thick italics (***B, P, S, Cl***). The large gaps between didymium and tantalum, bismuth and uranium, are not filled up for want of sufficient data. The hypothetical assumptions for the remaining curves are justified by further considerations. The molecular volumes for hydrogen, oxygen, and nitrogen in the gaseous state, as determined by means of transpiration [1] and the comparison of the molecular volumes of the solid compounds of fluorine and titanium with the molecular volumes of analogous compounds, show that the elements H, N, O, Fl, and Ti have, in the solid state, at any rate, approximately the atomic volumes which are ascribed to them in the table. R. Pictet [2] has shown that liquid oxygen has nearly the same density as water. In the diagram the density of solid oxygen is represented as somewhat greater than that of water. Cailletet and Hautefeuille [3] have calculated the density of oxygen, nitrogen, and hydrogen from the density of their solutions in liquid carbonic anhydride; they make the density of these bodies to be smaller, and consequently the atomic volumes become larger, than the values given in the table. Their experiments show these values to be greatly influenced by temperature.

[1] *Lieb. Ann.* 1867, Suppl. v. 129.

[2] *Liquéfaction de l'Oxygène*, Genève, 1878, 67; also J. Offret, *Ann. Chim. Phys.* 1880, xix. 271; *Wied. Beibl.* 1880, iv. 417.

[3] *Compt. Rend.* 1881, xcii. 1086.

The shape of the curves shows that the space occupied by the isolated elements in the solid state is a periodic function of their atomic weights.[1]

The atomic volumes regularly increase and diminish with the increasing atomic weights. The curve which represents these changes is divided by five maxima into six sections, which exhibit the form of a series of chains placed in a row. There is a strong resemblance between the second and third, and also the fourth and fifth. These sections correspond to almost equal lengths of the axis of the abscissæ.

If the missing portions of the curve between didymium and tantalum, and bismuth and thorium were completed by sections analogous to those between vanadium and niobium, and between arsenic and zirconium, eight sections would be formed. The first and last, however, only form half a curve

The position of an element on this curve is closely connected with its physical and chemical properties, so that similar elements occupy corresponding positions on similar portions of the curve. It is not very remarkable that the maxima of the curves are formed by light metals, and the lowest minima by heavy metals, since it has long been known that the former have very large and the latter very small atomic volumes. But it is very remarkable that elements with similar atomic volumes exhibit very different properties, depending as to whether their position is on a rising or falling branch of the curve, which position is determined by the given element having a larger or smaller atomic volume than the element with the next larger atomic weight. P and Mg, Cl and Ca, Nb and In, Mo and Cd are examples of the truth of this

[1] The space occupied by elements in compounds is also undoubtedly a function of their atomic weight, but the nature of this function cannot at present be generally stated. Although our knowledge of the space occupied by the different atoms in a molecule is uncertain, we may, however, assume with tolerable accuracy that the difference between the space occupied by different elements is, as a rule, smaller in compounds than in the isolated condition. For example, the oxides of the light metals occupy a smaller, and the oxides of the heavy metals a larger space than the quantity of metal contained in them. There is a much smaller difference between the volumes of the oxides of the light metals than there is between the atomic volumes of the metals themselves. In the heavy metals the difference between the volumes of the oxides is often the same as the difference between the volumes of the metals themselves.

proposition. The difference in the properties and character of the elements is partly indicated in the table.

§ 64. Only those elements exhibit the property of malleability which lie in a maximum or minimum of the curve, or immediately follow a maximum or minimum. The light malleable metals occupy the points of maxima and the contiguous portions of the descending curves (Li, Be; Na, Mg, Al; K, Ca; Rb, Sr; Cs, Ba). The heavy malleable metals are found in the lowest points of sections IV., V., VI., and VII., and in the adjacent sections of the ascending curves (Fe, Co, Ni, Cu, Zn; Rh, Pd, Ag, Cd, In, Sn; Pt,[1] Au, Hg, Tl, Pb). The sections I., II., and III. do not contain any heavy metals.

The brittle heavy metals and semi-metals are found in IV., V., and also in VII. (if Os is really smaller than Au), shortly before the lowest points on the descending curves (Ti, V, Cr, Mn; Zr, Nb, Mo, Ru; Ta, W, Os, Ir).

Non-metallic and semi-metallic (*i.e.* brittle, but possessing metallic lustre) elements are found in each section on the ascending branches of the curve preceding the maximum. In II. and III. they occupy the whole of the curve from minimum to maximum (B, C, N, O, Fl; Si, P, S, Cl), but in IV., V., and VII. they are found on the ascending portions of the curve near the maxima (As, Se, Br; Sb, Te, I; Bi).

§ 65. According to Bottone[2] the hardness of elements is inversely proportional to their atomic volume. But his statement must be received with caution, since he found that his rule held good for indium, although he had made use of the incorrect atomic weight In=74 in his calculations. He also wrongly assumes that calcium is softer than sodium, &c.

§ 66. The fusibility and volatility of the elements are also closely connected with their atomic weights and atomic volumes.

Owing to the difficulty of determining the melting points of very volatile and also of very infusible elements, the melting points of many of them are still unknown. And although in addition to this, widely different results have

[1] Assuming, as stated in § 61, that the atomic weight of osmium is less than that of iridium, and that the atomic weight of ruthenium is smaller than that of rhodium.

[2] *Mondes*, xxxi. 720; *Sill. Amer. Journ.* 1873, 457.

been obtained by different investigators in determining melting points, the approximate knowledge we possess is sufficient to prove the connection between the fusibility of an element and its atomic weight.

The following table, contained in a research by T. Carnelley,[1] shows as far as possible the melting points of the elements in absolute temperature (starting at −273° C.) The determinations of Violle[2] for the melting points of Cu, Ag, Pd, Ir, Pt, and Au are inserted. Carnelley[3] also prefers these numbers to older determinations. The melting point of bromine is corrected from the determination of J. Philipp,[4]

MELTING POINTS EXPRESSED IN ABSOLUTE TEMPERATURE.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.		
H 70?									
Li 453	Be *b* 1230	B *v h*	C *n f*	N *v h*	O *v l*	F *v l*			
Na 369	Mg[5] 1023	Al 1123	Si *v h*	P *r* 528 *c* 317	S 388	Cl 198			
K 335	Ca +Sr	Sc ?	Ti *n f*	V *n f*	Cr *b* 2270	Mn 2170	Fe 2080	Co 2070	Ni 1870
Cu 1330	Zn 690	Ga 303		As *a* 773	Se 490	Br 266			
Rb 311	Sr +Ba	Y ?	Zr +Si	Nb *n f*	Mo *v h*		Ru 2070	Rh 2270	Pd 1775
Ag 1230	Cd 590	In 449	Sn 503	Sb 710	Te 728	I 387			
Cs 300	Ba 748	La *a* 710,	Ce and	Di *b* 1273					
		Yb ?		Ta *n f*	W *v h*		Os 2770	Ir 2220	Pt 2050
Au 1310	Hg 234	Tl 563	Pb 599 Th ?	Bi 540	U −Fe				

N f = not fused; *v h* = very high; *v l* = very low; *a* = above; *b* = below; + higher than; − lower than; and in the case of phosphorus *r* = red, and *c* = colourless.

[1] *Phil. Mag.* [5], viii. 315.
[2] *Compt. Rend.* lxxxix. 703.
[3] *Chem. Soc. Jour.* 1880, 126.
[4] *Ber. d. deut. chem. Ges.* 1879, 1424.
[5] Mg melts below 1070° (absolute temperature) according to V. Meyer, *Ber. d. deut. chem. Ges.* 1887, 498.

that of caesium from Setteberg's determination;[1] and the melting point of hydrogen is from Pictet's experiments[2] given at −200° C., or 70° absolute temperature.

The contents of this table are graphically represented in Figure II. of the table affixed to the end of this book, in which the atomic weights are represented by abscissæ, and the melting points by ordinates. Where the melting points have not been accurately determined they are represented by dotted lines, and in the case of the very difficultly fusible elements these lines are prolonged to the top of the table. A comparison of the curve uniting the extremities of the ordinates with the curve for the atomic volumes shows great similarity to exist. Both are divided by maxima into corresponding sections. The two curves do not, however, coincide, but the curve for the melting point appears to be displaced to the right, so that its maxima coincide with the third or even fourth element after the maxima of the atomic volumes, *e.g.* C, Si, Ti or V, Zr, or Nb and Ta. The minima occur immediately before the maxima of atomic volume, *e.g.* before hydrogen and the elements of the chlorine group, or perhaps their nearest associates; in the II. period before N or O, and the minimum point of fusibility is probably identical with Cs, *i.e.* the maximum of volume itself, in V.

In the larger sections of the curves a second minimum occurs at the metals Ga, In, Hg.

All gaseous elements, and all those elements which fuse easily below a red heat, are found on the ascending portions and at the maxima points of the atomic volume curve. All infusible and difficultly fusible elements occur at the points of the minima and descending portions of the curve. The fusibility of the elements considered as a function of their atomic weight exhibits a periodicity corresponding to that shown by the atomic volume and the malleability.

Only those elements are easily fusible the atomic volume of which is larger than that of the element with the next smaller atomic weight. Those elements are difficultly fusible for which the reverse is the case.

[1] *Lieb. Ann.* 1882, ccxi. 115.

[2] *Liquéfaction de l'Oxygène*, 1878, 98.

Either a very easily fusible or an infusible element occurs between every two groups of easily and difficultly fusible elements. This connecting link is wanting only in the case of C and N, and between Si and P. Other relations are observed on comparing the elements on the corresponding points of the volume curve, or the elements forming a natural family in the perpendicular columns of the table on page 127. In most of these groups the fusibility decreases, or, in other words, the melting point rises, with increasing atomic weight. The melting point falls with an increase in the atomic weight only in the following groups: (1) the alkali metals, Li, Na, K, Rb, and Cs; (2) apparently in the case of the alkaline earths, Be, Mg, Ca, Sr, Ba, and certainly in the group of the heavy metals, Zn, Cd, and Hg. Here the higher members are more fusible than the lower. In the nitrogen-bismuth group the fusibility diminishes from nitrogen to arsenic, and increases from arsenic to bismuth. In the case of the noble metals the fusibility increases from copper to silver, and again decreases from the latter to gold.

Owing to these differences the various sections of the curve of melting points exhibit a certain amount of variation. For example, the difference between the melting points of the so-called halogens, F, Cl, Br, and the alkali metals, Li, Na, K, Rb, diminishes with the increasing atomic weights until it is reversed in the case of I and Cs, so that Cs melts more easily than iodine, Zn melts 387° C. higher than Gâ, Cd only 141° higher than In, but Hg 330° lower than Tl.

Similar variations are found in the relations between the neighbouring elements P, S, Cl; As, Se, Br; Sb, Te, I. The melting points of the sulphur group increase more rapidly with the atomic weight than the melting points of the chlorine group; they are always approximately double those of the latter.[1]

Cl 198°	Br 266°	I about 387°
S 388° = 2 × 194°	Se 490° = 2 × 245°	Te about 725° = 2 × 363°

§ 67. The compounds of the elements also exhibit relations in their melting points, which have recently been the

[1] Carnelley and Williams, *Chem. Soc. Jour.* 1879, 563; *Phil. Mag.* [5] viii. 1879, 320. The melting point of Te was then believed to be 773°, *i.e.* = 387 × 2.

subject of special investigation by Carnelley.[1] Thus the compounds of the metals of the alkalis and alkaline earths (columns I. and II. in table, page 120) with the elements of the chlorine group (column VII.) exhibit the following melting points, expressed in the ordinary degrees centigrade.

RX	R=Li	Na	K	Rb	Cs
X=F	801	902	789	753	?
Cl	598	772	734	710	630
Br	547	708	699	683	?
I	446	628	634	642	?

RX_2	R=Be	Mg	Ca	Sr	Ba
$X_2=F_2$	?	908	902	902	908
Cl_2	*circa* 600	708	719	825	
Br_2	*circa* 600	695	676	630	812
I_2	?	?	631	507	

These variations are pretty regular in the horizontal as well as in the vertical rows. In most cases the melting point sinks with an increase in the atomic weight of the negative or positive element. It only rises between the first and second metals. Strontium and barium in the second table also exhibit an abnormal behaviour.

The chlorides, bromides, and iodides of boron, aluminium, and the other metals in column III. (page 120), are more easily fusible, and more volatile when sufficiently stable, than the above compounds. These compounds of boron are liquid at the ordinary temperature, and the compounds of aluminium melt as follows:

Al_2Cl_6	Al_2Br_6	Al_2I_6
Very low temperature.	90° C.	185°

From this relationship Carnelley [2] concludes that beryllium chloride (m. p. 600° *circa*) does not belong to this group of compounds, and therefore has not the composition $BeCl_3$ or Be_2Cl_6. The atomic weight of beryllium cannot, therefore, be half as large again as given on page 120. This conclusion

[1] See the papers which have appeared since 1876 in different numbers of the *Chem. Soc. Journ.*, *Roy. Soc. Proc.* and *Phil. Mag.*

[2] *Phil. Mag.* 1879, 371.

is justified by the fact that Carnelley [1] was enabled to calculate with approximate accuracy the melting points of beryllium chloride and bromide, before they had been experimentally determined, by the aid of the rules founded upon the variations in the melting points of compounds with the variations in the atomic weights.

He found the following values :

	Calculated	Observed
$BeCl_2$	between 547 and 597,	between 585 and 617.
$BeBr_2$	,, 529 and 547,	,, 585 and 617.

In the same way, L. Meyer calculated the melting point of Cs. The calculation has been confirmed by Setterberg's determination of the melting point.

§ 68. Volatility is intimately associated with fusibility. Only those easily fusible metals are volatile which are found on the ascending portions of the curve for atomic volumes. Whilst the elements on the ascending portions of III. and IV. are gaseous or easily volatile, many which occupy a similar position in IV. and V. require a strong red heat, or even a white heat, for volatilisation.

The following table shows the absolute temperature of the boiling points of these elements under a pressure of one atmosphere, arranged according to the sections of the curves, and in the same order in which they appear on the curve.

Table of Boiling Points.

I.	H *b* 70 ?						Li
II.				N *b* 70 ?	O *b* 70 ?	F *b* 100 ?	Na 1130–1230
III.				P 563	S 720	Cl 240	K 900–1000
IV.	Zn 1200	Ga ?		As 700 ?	Se 938	Br 331	Rb ?
V.	Cd 1045	In ?	Sn 1870–2070	Sb 1360–1870	Te *b* 1600	I 487	Cs ?
VI.	Hg 630	Tl ?	Pb 1870–2070	Bi 1360–1870			

[1] *Proc. Roy. Soc.* 1879, No. 197 ; *Chem. Soc. Journ.* 1880 (*Trans.*) 127.

These imperfect data show the variations between the boiling points to resemble those exhibited by the melting points. In most families the boiling point appears to increase with the atomic weight, but in both the groups occupying the beginning and end of the ascending curves, viz. the alkali metals and the zinc group, the reverse is the case.

The fusible elements occurring on the ascending curves can be more or less easily volatilised within artificially attainable temperatures, but the difficultly fusible elements occurring on the descending curves and at the minima cannot be perceptibly volatilised by the highest temperatures, which can be attained artificially.

Silver, one of the metals which connects the difficultly with the easily fusible elements, and which occurs at the commencement of an ascending curve, can be distilled at a white heat.[1]

It is possible that the other metals occupying the mean position between the easily and difficultly fusible metals are not exceedingly difficult to volatilise; but observations suitable for deciding the question have not yet been made.

The preceding relations between atomic weight, atomic volume, fusibility, and volatility may be expressed by the following proposition:

Every element is easily fusible and volatile which possesses a greater atomic volume than the immediately preceding element with a lower atomic weight: its molecules can be easily separated. Inversely, each element is with difficulty fusible or volatile the atomic volume of which is smaller, or not larger than that of the preceding element, having a smaller atomic weight. All those elements melt and volatilise easily the atomic volumes of which would be diminished, if it were possible, by reducing their atomic weights to convert them into the element with the next lower atomic weight. On the other hand, those elements fuse and volatilise with difficulty the atomic volumes of which would be increased, if it were possible, by reducing their atomic weights to convert them into the element immediately preceding.

This simple relation is obviously produced by a definite

[1] For the distillation of silver, see Stas, *Nouvelles Recherches*, 36.

and probably simple cause, which has, however, not yet been discovered.

§ 69. Ductility, fusibility, and volatility of the elements are closely connected with their internal structure, especially with their crystalline form and expansion by heat. These are, therefore, also periodic functions of the atomic weight. So far as the very scanty observations indicate, the ductile metals occurring at and near the highest and lowest points of the curve for atomic volumes crystallise in the regular system. This has been proved to be the case with a greater or lesser degree of certainty for Na, Mg, Al; K, Fe, Co, Ni, Cu; Pd (? dimorphous), Ag; Pt, Ir, Au, Hg, Pb. The non-metals standing at the lowest portions of sections II. and III. of the curve also crystallise in the regular system C (as diamond, dimorphous), Si and P (colourless, dimorphous). On the other hand, the volatile and more or less brittle elements found on the ascending curves do not crystallise in the regular system, but in several other systems. This has been proved to be the case for P (red), S, Zn,[1] As, Se; Cd, In, Sn, Sb, Te, I. The crystalline form of the brittle metals occurring on the descending curves is hardly known; some of them, at least, do not appear to crystallise in the regular system, *e.g.* Zr.

§ 70. The researches of Fizeau show that the volatile elements occurring on the ascending curve possess, almost without exception, a larger coefficient of expansion by heat between 0° and 100° than the difficultly fusible elements occupying the minimum.

T. Carnelley[2] asserts that the coefficient of expansion of an element increases as the melting point sinks.

H. F. Wiebe,[3] starting from theoretical speculations, arrived at the conclusion that the cubic coefficient of expansion a is inversely proportional to the amount of heat which

[1] According to the investigation of Fizeau, *Compt. Rend.* 1869, lxviii. 1125; *Pog. Ann.* cxxxviii. 26; Strecker, *Jahr. Ber.* 1869, lxxxiv., zinc does not belong to the regular system, as was formerly believed to be the case. It expands unequally in different directions under the influence of heat.

[2] *Ber. d. deut. chem. Ges.* 1878, 2289.

[3] *Ibid.* 1879, 788.

is required to raise the atomic weight A from the melting point σ to the boiling point s; thus, if c = the specific heat, a is inversely proportional to the product

$$A\ c\ (s - \sigma);$$

therefore $A\ c\ (s - \sigma)\ a = \text{const.} = C.$

A comparison with experimental results gave, according to Wiebe's calculation:

A	c	s	σ	a	$\frac{1}{c}$
S = 31·98	0·1710	447	113·6	0·0002670	2·05
Se = 78·0	0·0801	700	217	0·0001696	2·02
P = 30·96	0·1900	278	44·5	0·0003556	2·04
Hg = 199·8	0·0333	356	−40	0·0001882	2·02

The author calls attention to the fact that unknown boiling points can be calculated by means of the above formula, or by the aid of a corresponding formula containing the coefficient of linear expansion, *e.g.*:

	Melting point	Boiling point
Ag	916°	1870°
Au	1037°	2240°

It is, however, doubtful whether this rule is correct, as Carnelley [1] has found the boiling points of tin, lead, antimony, and bismuth to differ considerably from the results calculated by Wiebe's formula.

Wiebe [2] afterwards proposed another rule, viz. that the heat required to raise the atomic weight of an element from absolute zero to the temperature of its melting point, *i.e.* the total amount of heat contained in the atom before it melts, is almost inversely proportional to its coefficient of cubical expansion, the product of these two values must consequently be approximately the same for different elements.

Let A be the atomic weight, c the specific heat, T the absolute temperature of the melting-point, and β the coefficient of cubical expansion; then A, c, T, β = constant.

[1] *Chem. Soc. Journ.* 1879 (*Trans.*) 565.
[2] *Ber. d. deut. chem. Ges.* 1880, 1258.

This holds good for a series of elements, especially for those crystallising in the regular system, but there are many exceptions to the rule.

Raoul Pictet [1] has proposed another mode of representing the relation between melting point, expansion, and atomic volume.

Starting from the hypothesis that the mean value of the amplitude of vibration of the particles of solid bodies (at the moment of melting), oscillating about their point of equilibrium, must be equal for all bodies, he arrives at the conclusion that the product of the mean distance of the particles and the coefficient of linear expansion will be proportional to the absolute temperature of the melting-point, and the product of these three values is constant.

Since the absolute distance between the particles is not known, the corresponding cube root of the atomic volume may be substituted in its place.

$$\text{Then } a \,.\, T \sqrt[3]{V} = \text{const.}$$

where a is the coefficient of linear expansion, T the melting-point calculated from the absolute zero, and V the atomic volume, or the quotient of the atomic weight A by the density D. The melting points in column V. of the accompanying table are mostly contained in Carnelley's table. The numbers which Violle obtained for Cu, Pd, Ag, Ir, Pb have been added. Where Pictet used different numbers both values are given; they are distinguished by prefixing the initials of the names of the investigators. Column VI. contains the values of linear expansion from 0° to 100°, *i.e.* one hundred times the value of the mean coefficient of expansion for 1° C. Fizeau's numbers are distinguished by F, and those employed by Pictet by P.

[1] *Compt. Rend.* 1879, lxxxviii. 855; *Synthèse de la Chaleur.* Genève, 1879, 15.

I.	II. A	III. D	IV. V	V. T	VI. α	VII. $\alpha TV^{\frac{1}{3}}$
Mg [1] .	23·94	1·74	13·8	1020 *C*	0·00259 *F*	6·6
Al [1] .	27·0	2·56	10·6	1120 *C*	231 *F*	5·7
				870 *P*	222 *P*	4·3
S . .	31·98	2·04	15·7	388 *C*	[2] 641 *F*	(6·2)
Fe [3] .	55·9	7·8	7·2	2080 *C*	119 *F*	4·8
				1870 *P*	118 *P*	4·3
				1770 *P*	„ *P*	4·0
Co [3] .	58·6	8·5	6·9	2070 *C*	124 *F*	4·9
				1770 *P*	„	4·2
Ni [3] .	58·6	8·8	6·7	1870 *C*	128 *F*	4·5
				1720 *P*	„	4·1
Cu . .	63·2	8·8	7·2	1330 *C*	168 *F*	4·3
				1320 *P*	172 *P*	4·4
Zn [4] .	64·9	7·15	9·1	676 *C*	292 *F*	4·1
				685 *P*	297 *P*	4·3
				723 *P*	294 *P*	4·4
Se [1] .	78·9	4·6	17·1	490 *C*	368 *F*	4·7
Ru [5] .	103·5	12·3	8·4	2070	096 *F*	4·1
Rh [5] .	104·1	12·1	8·6	2270	085 *F*	4·0
Pd [6] .	106·2	11·5	8·2	1775	118 *F*	4·4
					100 *P*	4·1
Ag [1] .	107·66	10·5	10·2	1230 *C*	192 *F*	5·5
				„	191 *P*	5·5
				„	162 *P*	4·6
Cd [4] .	111·7	8·65	12·9	593 *C*	307 *F*	4·5
					313 *P*	4·4
In [1] .	113·4	7·42	15·3	449	417 *F*	4·6
Sn [7] .	117·8	7·29	16·1	503 *C*	223 *F*	2·8
				508 *P*	293 *P*	3·8
				„	306 *P*	3·9
Sb [8] .	120·0	6·7	17·9	710	169 *F*	(3·2)
Sb [9] .				„	115 *F*	(2·2)
Sb [10] .				„	088 *F*	(1·6)
				„	179 *P*	(3·4)
				„	330 *P*	(6·2)
Te [1] .	126·0	6·25	20·2	773	168 *F*	3·5
				798	„	3·6
Os [5] .	195·0	22·5	8·8	2770	066 *F*	3·8
Ir [1] .	192·7	22·4	8·6	2223	070 *F*	3·6
					068 *P*	3·9
Pt [1] .	194·0	21·5	9·1	2048	090 *F*	3·9
					088 *P*	3·8

[1] Fused.

[2] Coefficient of expansion of a rhombic crystal of sulphur, for a plane at an angle of 54° 44′ to the three axes.

[3] Reduced by hydrogen and compressed. [4] Distilled.

[5] Semi-fused. [6] Hammered. [7] Compressed powder.

[8] Coefficient of expansion in the direction of the axes.

[9] Coefficient of mean expansion.

[10] Coefficient of expansion at right angles to the axes.

I.	II. A	III. D	IV. V	V. T	VI. α	VII. $\alpha TV^{\frac{1}{3}}$
Au . .	196	19·3	10·2	1310 *C*	0·00144 *F*	4·1
				1370 *P*	„ *P*	4·3
				„	148 *P*	4·4
				„	151 *P*	4·5
Tl [1] .	203·7	11·86	17·1	563	302 *F*	4·4
					314 *P*	4·5
Pb [1] .	206·4	11·38	18·1	605 *C*	292 *F*	4·6
				608 *P*	285 *P*	4·5
				„	287 *P*	4·6
Bi [2] .	207·5	9·82	21·1	538 *C*	162 *F*	(2·41)
Bi [3] .					135 *F*	(2·05)
Bi [4] .					121 *F*	(1·84)

In accordance with Pictet's hypothesis, the products in column VII. are approximately equal (4–5) for most of the elements. The products are not quite equal, since the coefficient of expansion varies with the temperature, and in these calculations the expansion between 0° and 100° was used instead of the coefficient of expansion between the absolute zero and the melting point. The great differences exhibited by such elements as S, Sb, Bi, which expand differently in different directions, is easily explained. Tin and tellurium also give too low results, the former because it was only investigated by Fizeau in the form of compressed powder. Mg, Al, Ag, yield too high results; this is, however, not the case for the two latter, if Pictet's numbers are used in the calculation.

§ 71. Since Pictet's rule applies to most elements, unknown melting points may be calculated by means of a formula, deduced from this rule, viz.

$$T = \frac{4{\cdot}5}{a \cdot \sqrt[3]{V}}.$$

This gives the following results for silicon and graphite:

	A	D	V	α	T
Graphite	11·97	1·88	6·4	0·000786	3200°
Silicon	2·8	2·49	11·2	763	2660°

These numbers are probably tolerably accurate.

[1] Fused.
[2] Coefficient of expansion in the direction of the axes.
[3] Coefficient of mean expansion.
[4] Coefficient of expansion at right angles to the axes.

On the other hand, Fizeau found that sublimed arsenic, composed of a confused mass of crystals, has a small coefficient of expansion, viz. 0·000559, showing that it must have a very high melting point, but Landolt [1] has proved that arsenic can be melted in closed vessels at a dull red heat. It is obvious that As does not obey Pictet's rule any more than antimony and bismuth. Substances crystallising in the regular system may also form exceptions. Carbon, crystallising in the regular system as diamond, possesses the smallest expansion of all the elements between 0° and 100°; it is only 0·000118. Fizeau [2] has shown that it varies greatly with the temperature. It diminishes rapidly with a falling temperature, until it disappears at −42·3°, where the density of the diamond attains its maximum, like water does at 4°, cuprous oxide at −4·3°, and beryll. −4·2°. It is obvious that a varying value cannot be of any use in calculating the melting point.

The slight and variable expansion of the diamond is undoubtedly connected with its small specific heat (§ 38); this is, however, scarcely the sole cause. It is not probable that carbon alone should exhibit such a peculiarity; on the contrary, it is very possible that other elements behave similarly only at different temperatures. The relation of expansion to atomic weight can only be properly understood when the expansion of the metals within wide limits of temperature has been measured.

§ 72. The refraction of light by the elements and their compounds is also essentially related to the atomic weight; but here also very little is known concerning the causal connection.

The investigations of Gladstone and Dale,[3] Landolt,[4] and Wüllner [5] show that the value $n-1$, generally known as the

[1] Kopp and Will, *Jahresber. d. Chemie*, 1859, 182.

[2] *Compt. Rend.* 1865, lx. 1161; 1866, lxii. 1101 and 1133; *Ann. Chim. Phys.* [4] viii. 335; *Pogg. Ann.* cxxvi. 611; cxxviii. 564.

[3] *Phil. Trans.* 1858 and 1863; *Phil. Mag.* [4], xvii. 222, xxvi. 484; *Chem. Soc. Journ.* 1870, 101 and 147.

[4] *Pogg. Ann.* 1862, cxvii. 353; 1864, cxxii. 545, cxxiii. 595; *Lieb. Ann.* 1865, Suppl. iv. 1.

[5] *Pogg. Ann.* 1868, cxxxiii. 1–53.

refractive power,[1] in the case of liquids, varies with the temperature in the same way as the density d, hence the relation between the two, $\frac{n-1}{d}$, which is known as the specific refractive power, is independent of the temperature.

This assumption is approximately but not absolutely correct, when n represents the index of refraction for homogeneous light of a particular colour, or more correctly for A, a ray of infinite wave length, which can be calculated by Cauchy's formula,

$$n = \mathrm{A} + \frac{\mathrm{B}}{\lambda_2} + \frac{\mathrm{C}}{\lambda_4} + \ldots$$

or any similar interpolation formula.

The investigations of Gladstone and Dale, as also those of Landolt, further show that the specific refraction of a liquid can be calculated from the specific refraction of its constituents by means of the formula;

$$\frac{\mathrm{N}-1}{\mathrm{D}} \cdot \mathrm{P} = \frac{n_1-1}{d_1} \cdot p_1 + \frac{n_2-1}{d_2} \cdot p_2 + \frac{n_3-1}{d_3} \cdot p_3 + \ldots$$

where N represents the index of refraction and D the density of the whole liquid, n_1, n_2, n_3, &c., the refractive indices, d_1, d_2, d_3, &c., the densities of its individual constituents, p_1, p_2, p_3, &c., the weight of the different constituents contained in the weight P of the mixture or compound. This rule is not absolutely correct, but it is more or less approximate for homogeneous chemical compounds, and mixtures of chemical compounds. When P equals the molecular weight of a compound,

e.g. $$\mathrm{P} = \mathrm{M} = x\,\mathrm{A}_1 + y\,.\,\mathrm{A}_2 + z\,.\,\mathrm{A}_3 + \ldots$$

then the preceding formula becomes

$$\frac{\mathrm{N}-1}{\mathrm{D}} \cdot \mathrm{M} \cdot = x\,\frac{n_1-1}{d_1} \cdot \mathrm{A}_1 + y \cdot \frac{n_2-1}{d_2} \cdot \mathrm{A}_2 + z\,\frac{n_3-1}{d_3} \cdot \mathrm{A}_3 + \ldots$$

[1] Formerly n^2-1 was termed the refractive power and $\frac{n^2-1}{d}$ the specific refraction, but H. A. and L. Lorenz have recently replaced the latter expression by $\frac{n^2-1}{(n^2+2)d}$, which has been proved by experiment to be independent of temperature.

where A_1, A_2, and A_3 represent the atomic weights of the constituents, and x, y, z the number of atoms contained in the molecule M. The product of the specific refraction into the atomic weight is called the refraction equivalent of the given element; the product of the specific refraction into the molecular weight is called the molecular refraction, or the refraction equivalent of the compound.[1]

The meaning of the above formula may be thus expressed. The molecular refractive power of a compound is equal to the sum of the refraction equivalents of its constituents. This proposition is not however absolutely true.

The refraction equivalents of some of the elements cannot be directly determined, and it is also doubtful whether their values in the solid state remain unchanged by their transition to liquid compounds. As a rule, the refraction equivalents of the elements have been calculated from the molecular refraction of a large number of their compounds. Let R*fa* (M) be the equivalent of refraction of a compound, having the molecular weight (M) for the red hydrogen line *a*, and let R*fa* (C), R*fa* (H), &c., be the refraction equivalents of the elements, then for the compound $C_n H_{2m} O_p$, we obtain the equation $\mathrm{R}fa\ (C_nH_{2m}O_p) = \frac{N-1}{D} \cdot M = n.\mathrm{R}fa\ (C) + 2m\mathrm{R}fa(H) + p\mathrm{R}fa(O)$. Having determined the molecular refraction of a large number of compounds of carbon, hydrogen, and oxygen for the three hydrogen lines *a* (red), β (green), Fraunhofer's C and F, and γ (blue) near Fraunhofer's G, Landolt was able to calculate the refraction equivalents of the elements contained in these compounds.[2]

At the suggestion of Landolt, A. Haagen[3] has by a similar method determined the refraction equivalents of ten other elements, and has also calculated from these observations the refraction equivalent R*fa* for the constant A by means of Cauchy's dispersion formula.

[1] Landolt, *Pogg. Ann.* 1864, cxxiii. 600.
[2] *Pogg. Ann.* 1864, cxxiii. 621; *Lieb. Ann.* 1865, Suppl. iv. 18.
[3] *Pogg. Ann.* 1867, cxxxi. 117.

TABLE OF REFRACTION EQUIVALENTS.

Element	R/A	R/α	R/β	R/γ
H	1·29	1·302	1·316	1·319
O	2·90	2·76	2·82	2·83
C	4·86	5·06	5·17	5·25
Cl	9·53	9·80	—	—
Br	14·75	15·34	—	—
I	23·55	24·87	—	—
S	14·74	16·03	—	—
P	14·60	14·93	—	—
As	18·84	20·22	—	—
Sb	—	25·66	—	—
Sn	18·64	19·89	—	—
Si	7·81	7·90	—	—
Na	4·71	4·89	—	—

If these values were strictly available for all compounds it would be possible to calculate from the known composition of any compound of the three elements named, its molecular refraction, or to calculate the composition of a compound from its molecular refraction.

But Landolt found that the calculated values only agreed with a portion of the experimental observations, whilst in other cases considerable deviations existed. This arises from the fact that not only the nature but also the arrangement of the atoms exerts an influence on the molecular refraction of compounds. This will be further discussed in section VII., which treats of the linking of atoms.

Gladstone and Dale arrived at the same conclusion. The former determined the refraction equivalents of most of the elements, but in many cases with doubtful accuracy. He concludes from his investigations [1] that a single value for the refraction equivalent of any element is not sufficient to explain the optical behaviour of chemical compounds, but, on the other hand, two different refraction equivalents must be assumed for many elements, according to the kind of compound in which they are contained.

In the accompanying table the elements are arranged in the horizontal rows in the order of their atomic weights. Gladstone's values of the refraction equivalents for the line A [2]

[1] *Lond. Roy. Soc. Proc.* 1869, xviii. 49, and 1881, xxxi. 327; *Lond. Phil. Trans.* 1870, clx. 9.

[2] *Chem. Soc. Jour.* 1870, 109.

in the red portion of the solar spectrum are given under the atomic symbols of the elements.

This table exhibits similar relations to the others. Within each period in which the other properties have one or two maxima, the index of specific refraction and the refraction equivalent also exhibit one or two maxima. Nearly all the maxima in the latter case occur in the (vertical row) carbon or nitrogen groups. In some of the horizontal rows in the table a second less marked maximum occurs. A detailed discussion of these numbers is useless on account of the uncertainty attached to the determination of many of these refraction equivalents. It is sufficient to have proved that the refraction equivalent is a function of the atomic weight.

					H	Li	Be	B	C
					1·3[1] 3·5[2]	3·8	5·7	4·0	5·0
N	O	F				Na	Mg	Al	Si
4·1[3] 5·3[4]	2·9	1·4?				4·8	7·0	8·4	7·5[5]? 6·8[6]
P	S	Cl				K	Ca	—	Ti
18·3	16·0	9·9[7] 10·7[8]				8·1	10·4		25·5?
V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	—
25·3?	15·9[9] 23·0[10]?	12·2[11] 26·2[12]?	12·0[13] 20·1[14]	10·8	10·4	11·6	10·2		
As		Br				Rb	Sr	Y	Zr
15·4		15·3[15] 16·9[16]				14·0	13·6		22·3?

[1] In organic compounds.
[2] In HCl, HBr, HI.
[3] In NO, N_2O, CN, NH_3, &c.
[4] In nitrites and nitrates.
[5] In chlorides.
[6] In the oxide, &c.
[7] In organic compounds.
[8] In solutions of its salts.
[9] In salts of the sequioxide.
[10] In chromates.
[11] In manganous salts.
[12] In permanganates.
[13] In ferrous salts.
[14] In ferric salts.
[15] In organic compounds.
[16] In solutions of the salts.

Nb	Mo	—	Ru	Rh	Pd	Ag	Cd	In	Sn
				24·2?	22·2	13·5	13·6		27·0 19·2[1]
Sb	Te	I				Cs	Ba	Ce	
24·5		24·5[2] 27·2[3]				13·7?	15·8	20·4?	
							Ng		
								Yb	
Ta	W	—	Os	Ir	Pt	Au	Hg	Tl	Pb
					26·0	24·0	21·3 29·0[4]	21·6?	24·8
Bi	—	—							Th
39·2									

Landolt[5] has pointed out that different values are obtained for the refraction equivalents if the new formula $Rf = \frac{n^2-1}{(n^2+2)d}p$ is employed instead of $Rf = \frac{n-1}{d}p$; but the mutual relation between the numbers remains unchanged, as the following calculations of Landolt show:

	$\frac{n-1}{d}p$		$\frac{n^2-1}{(n^2+2)d}p$	
Element	R/A	R/a	R/a	R/A
H	1·29	1·30	1·02	1·04
C	4·86	5·06	2·43	2·48
Cl	9·53	9·80	5·89	6·02

According to Bayley,[6] the power of forming coloured compounds is also a periodic function of the atomic weight.

[1] In $Sn Cl_4$.
[2] In organic compounds.
[3] In solutions of its salts.
[4] In double iodides.
[5] *Berl. Akad. Sitz.-Ber.* 1882, 64; *Math. nat. Mitth.* ders., 43.
[6] *Phil. Mag.* 1882, xiii. 34. *Vide* curve of atomic volumes.

Colourless acids only form coloured salts with the oxides of those metals which occur near the minimum of atomic volumes.[1]

§ 73. The specific heat also, as shown more fully in section III., represents a function of the atomic weight; but it is not a periodic function, since, according to the law of Dulong and Petit, the specific heats are inversely proportional to the atomic weights. The atomic heat $A.c$ is to some extent dependent not only upon the atomic weight, but also upon the atomic volume. All elements which at a mean temperature do not obey or only approximately follow the law of Dulong and Petit possess not only small atomic weights but large atomic volumes also. All these elements occur in the sections I., II., and III., near the minima of the curve of atomic volumes. Lithium and sodium, elements possessing small atomic weights but large atomic volumes, occur in these sections also; and further, in the same sections, are the elements chlorine and potassium, possessing large atomic volumes. All these elements obey the law of specific heats. They are separated from the other elements by a line in the diagram of the curve of atomic volumes, called the limit of the law of Dulong and Petit. The elements lithium, sodium, chlorine, and potassium, which occur above this line, obey the law, whilst the specific heats at low temperature of the elements below this line have been found to be too low. Hence, in order that the law of specific heats may hold true even at low temperatures, it is necessary that elements with low atomic weights should possess atomic volumes of a certain magnitude. This fact is expressed empirically as follows: All elements possessing atomic weights less than forty times that of hydrogen obey the law of Dulong and Petit when their density, compared with that of water, is less than 1·5 (about).

It is also probable that the atomic heat of elements with larger atomic weights is influenced by the magnitude of their atomic volumes. The majority of determinations hitherto made are not, however, sufficiently exact or reliable to exhibit the nature of a variation which is in all probability but small.

§ 74. The conductivity for heat and electricity of the elements is, as is well known, dependent upon their ductility

[1] *Vide* Carnelley on this subject, *Ber. d. deut. chem. Ges.* xvii. 2151.

and malleability, and hence, like these, is a periodic function of the atomic weight, the periodicity of which coincides with that of the atomic volumes. Hence, from potassium upwards, the two periods of ductility and conductivity coincide with one of the atomic volumes.

Up to the present time all experiments[1] show that the best conductors of heat and electricity are the three metals silver, copper, and gold, the atomic weights of which show them to form as it were the points of transition between the elements difficult of fusion and those easily fusible and volatile. The observations in the case of other metals differ considerably, the differences being in all probability due to the impurities[2] of the substances employed and the lack of continuity in the wires used. Nevertheless all observers agree that the metal aluminium is closely allied to the three metals mentioned above. Aluminium also occupies on the curve of atomic volumes a similar position to that occupied by these metals. Next to these follow two groups of metals differing but little in their conductivity. The first group contains the three easily fusible and volatile heavy metals, zinc, cadmium, and tin, which by their atomic weights are nearly associated with silver and copper. To this group the metal indium will in all probability be found to belong. The second group contains three metals possessing maximum atomic volume and the adjacent light metals, lithium, sodium, magnesium, potassium, and calcium. Next to these groups come the ductile and difficultly fusible heavy metals, iron, nickel, palladium, and platinum. These metals have a minimum atomic volume, and possess a somewhat greater electrical resistance. The easily fusible and soft metals thallium and lead possess a lower conductivity than the members of this group.

It cannot escape notice that the brittle crystalline semi-metals, antimony, bismuth, and tellurium, which are only malleable within narrow limits of temperature, possess a lower conductivity than any of the above-mentioned metals. On the

[1] *Die Lehre vom Galvanismus*, by G. Wiedemann, 1861, i. 180; and 2nd ed. 1872, i. 292, contains an account of these observations.

[2] An account of the influence of small amounts of impurities is given in Wiedemann's *Galvanismus*, 1872, i. 299.

other hand, it is worthy of attention that mercury, which in the liquid state closely resembles these metals as regards their conductivity, is by reason of its atomic weight and volume nearly associated with zinc and cadmium, which are comparatively good conductors; further, mercury in the solid state is a malleable metal. These facts may be expressed in the following general rule:—The metals with large atomic weights occurring in section VII. of the curve of atomic volumes possess a lower conductivity than the corresponding metals occurring in sections IV. and V., which possess small atomic weights. Thus, according to the majority of observers,

Platinum	is not as good a conductor as			palladium, nickel, and iron.
Gold	,,	,,	,,	silver and copper.
Mercury	,,	,,	,,	cadmium and zinc.
Lead	,,	,,	,,	zinc.
Bismuth	,,	,,	,,	antimony.

In all probability thallium and indium will exhibit similar relations.

Matthieson found for the metal strontium, which occurs in section V., a conductivity only one third that of calcium. Its resistance is therefore greater than that of the brittle metal antimony. It would, however, be too rash to conclude from such observations that in the case of the light metals also, a low atomic weight is associated with a high conductivity. That this is really the case is by no means improbable, since potassium does not conduct as well as sodium, nor calcium as well as magnesium; lithium, on the other hand, which possesses the smallest atomic weight, is the worst conductor of these four metals.

The electrical conductivities of the difficultly fusible semi-metals which occur on the descending portions of the curves in sections IV., V., and VI. have not been ascertained; the non-metals on the ascending portions are either non-conductors or exceptionally bad conductors of electricity.

§ 75. The position of the elements in the series based upon the differences in their electrical potential is without doubt connected with their position in the series based upon the

atomic weights. The attempts hitherto made to arrange the elements, as regards their electrical behaviour, in a single series ranging from the most positive to the most negative elements have met with but questionable success. This fact is explained by the difficulties attendant on the observation and estimation of contact electricity. Although the formation of such a series still remains desirable, yet it is at present more important to know whether the electrical behaviour is related to the magnitude of the atomic weight.

The measurements of contact electricity[1] made by Kohlrausch, Gerland, and Hankel show, despite the small number of experiments, that this property exhibits variations similar to those of the atomic weights. The differences between the numbers placed under E in the following table represent the differences in potential produced by the contact of the metals in question, that produced by contact of zinc and copper being taken as 100. The homologous elements are placed in the same horizontal lines. Their electrical behaviour appears to vary with their atomic weights, and hence shows the desirability of further determinations.

	E		E		E		E
C = 11·97	78	Fe = 55·9	116	Pd = 106·2	85	Pt = 195	77
		Cu = 63·3	100	Ag = 107·66	88	Au = 197	90
		Zn = 64·9	200	Cd = 111·6	175	Hg = 199·8	119
Al = 27·2	225			Sn = 117·8	149	Pb = 206·4	156
				Si = 122·0	131	Bi = 207·5	130

The series based on the differences in their electrical potential[2] cannot be satisfactorily employed to replace the want of measurements for pure contact electricity. The values have been determined by comparing the electrical behaviour of the elements when each pair of them, either in direct contact or joined by a conductor of the first class, is placed in the same electrolyte or conductor of the second class. These determinations are at present too uncertain and unsystematic to be serviceable, and consequently yield very different arrangements

[1] *Vide* Wiedemann, *Galvanismus*, 2. Aufl. i. 21.

[2] A description of such electro-chemical series is given by Wiedemann in his *Galvanismus*, 1861, i. 40, 41; 2. Aufl. 1872, i. 58.

of the elements, without giving any clue to the cause of these differences.

If however such electro-chemical arrangements of the elements are disregarded and their general chemical behaviour, which is probably dependent on the former, be considered, then a periodicity is observed coincident with that of their other physical properties. These facts are noted on the curve of atomic volumes, at the end of the book, by the words 'electro-positive' and 'electro-negative.' These two properties exhibit variations similar to the alternations exhibited in malleability and brittleness.

In section I. of the curve of atomic volumes which terminates with lithium we have the strongly electro-positive element hydrogen only. In the descending portion of section II. of the curve, from the maximum to the minimum, are the strongly electro-positive elements lithium and beryllium, the hydrated oxides or hydroxyl compounds of which are strong bases. The elements boron, carbon, nitrogen, oxygen, and fluorine, which occur on the ascending portion of this section of the curve, from the minimum to the maximum, are mostly electro-negative; their hydrated oxides (and in the case of fluorine its hydrogen compound) are acids.

A similar relation is seen in section III. On the descending portion, from maximum to minimum, are the positive elements sodium, magnesium, and aluminium. This latter element also exhibits negative properties, its hydrated oxide possessing basic and feebly acid properties. Further on the ascending portions, from minimum to maximum, are the negative and acid-forming elements silicon, phosphorus, sulphur, and chlorine.

In sections IV. and V., the electro-chemical properties pass through two periods, whilst the atomic volumes pass through one only. In section IV., on the upper part of the curve, descending from the maximum, the positive elements potassium, calcium, and scandium occur, and in section V. the elements rubidium, strontium, and yttrium. Next follow the more or less negative elements in section IV.—titanium, vanadium, chromium, and manganese—and in section V. zirconium, niobium, molybdenum, and ruthenium. Some of

these elements are electro-positive; this is especially true of chromium and manganese, which thus form a link between these and the positive elements situated on the lower parts of the ascending curves, viz. in section IV., iron, cobalt, nickel, copper, zinc, and gallium; in section V., rhodium, palladium, silver, cadmium, and iridium. Then from this point to about the middle of the ascending curve follow strongly negative elements, viz. in section IV., arsenic, selenium, and bromine; and in section V., after tin, which may be regarded as positive as well as negative, follow antimony, tellurium, and iodine. And following these, without any intermediate elements, as in sections II. and III., is the strongly positive alkali metal caesium, which occupies the maximum.

In section VI., as in the others, first come the positive metals caesium, barium, lanthanum, didymium, and cerium; then follows a considerable gap in the series of atomic weights, the possibility of filling up which must at present be regarded as undecided. This blank is followed, in section VII., immediately before a minimum, by the negative elements tantalum and tungsten. To these the negative metal osmium may possibly be added; its atomic weight, though at present uncertain, cannot be greater, but must be less, than that of iridium. The elements iridium, platinum, and gold come next, exhibiting positive properties, and following them are the strongly positive elements mercury, thallium, and lead. These elements form the link between the metals on the upper portion of the curve and the almost negative element bismuth. Hence the changes in the chemical nature of the elements are similar in these sections to those in sections IV. and V.

§ 76. By comparing the elements on the corresponding parts of the different sections of the curve, it will be seen that the positive and negative characters are very differently developed. It is specially noticeable that in the neighbourhood of the minima of atomic volumes, the differences in chemical character are slight; but near the maxima the elements exhibit very marked differences. Thus the negative character of phosphorus, sulphur, and chlorine, of arsenic, selenium, and bromine; also the positive character of potassium and calcium, of rubidium and strontium, are much more distinctly marked

than are the negative characters of vanadium, chromium, and manganese, or of niobium, molybdenum, and ruthenium; or the positive characters of copper and zinc, of silver and cadmium.

Hence a condensation of mass in a small space does not appear to be conducive either to the development of a strongly negative or positive chemical character. The absolute value of the density and of the atomic volume can alone scarcely determine this. It is more probably influenced by the nature and manner of the changes in the atomic volume from element to element. The elements between which these changes are the greatest exhibit the greatest contrast in their chemical properties.

The magnitude of the atomic weight has apparently a visible influence upon the chemical character of the elements. This is especially noticeable in the higher members of the natural families of elements; the negative or acid-forming characters decreasing with increase in atomic weight. In the case of the halogen elements chlorine is more negative than bromine, and bromine than iodine; similarly sulphur is more negative than selenium, and the latter than tellurium; finally, phosphorus, arsenic, antimony, and bismuth exhibit similar gradations, phosphorus being the most negative; whilst indium, a metal corresponding to aluminium, has a certain tendency to act as a negative element, and tin possesses this property to a more marked degree; the metals lead and bismuth, which are associated with these and have large atomic weights, are essentially positive in character. Since in each of the above groups the atomic volume changes but slightly with increase in atomic weight, it appears in these cases that a high degree of density of the mass is not necessary to the development of a decided negative character. Remarks like the above will always be vague and uncertain so long as the positive and negative properties of the elements cannot be expressed numerically.

§ 77. That the magnetic and diamagnetic properties of the elements appear to be closely connected with their atomic weights and atomic volumes, has been mentioned in former editions of this book. Further, it was stated that those elements are usually magnetic the atomic volumes of which

approach the minima. It has been pointed out lately by Th. Carnelley[1] that, according to the determinations of Faraday, the elements placed in the same horizontal series in the table on p. 123 possess similar magnetic properties; and that the series are alternately magnetic and diamagnetic. The observations of different investigators in this matter do not agree well with one another;[2] a fact to be explained by the varying purity of the material employed. Hence at present it cannot be stated whether or to what extent the statement of Carnelley holds true. Should it be found to be correct, then the magnetic properties of the elements are also functions of their atomic weight. In the following tables the magnetic elements are denoted by the sign + attached to their symbols, the diamagnetic by the sign − and those in respect of which contradictory assertions have been made are denoted by the two signs ±.

MAGNETIC AND DIAMAGNETIC ELEMENTS.

H −																
Li ?	Be +	B ?	C +	N ±	O +	F ?				Na ±	Mg ±	Al ±	Si ±	P −	S −	Cl −
K +	Ca ?	Sc ?	Ti +	V ?	Cr +	Mn +	Fe +	Co +	Ni +	Cu −	Zn −	Ga ?		As −	Se −	Br −
Rb ?	Sr ?	Y +	Zr −	Nb −	Mo +		Ru ?	Rh ±	Pd +	Ag −	Cd −	In −	Sn −	Sb −	Te −	I −
Cs ?	Ba ?	La +	Ce +	Di +							Ng ?					
		Yb +		Ta −	W −		Os +	Ir ±	Pt +	Au −	Hg −	Tl −	Pb −	Bi −		
		Th ±			U ±											

Each of the horizontal series contains, on the left, magnetic elements, on the right, diamagnetic, and thus represents a period of the magnetic relations. These periods coincide with

[1] *Ber. d. deut. chem. Ges.* 1879, 1958.

[2] *Vide* Wiedemann's *Galvanismus*, 2nd ed. vol. II. i. 641; Ångström, *Ber. d. deut. chem. Ges.* 1880, 1465; L. Errera; *Bull. de l'Acad. Roy. de Belgique*, 1881. i. 313.

those of atomic volumes, save that the former contains two of the latter. As far as may be concluded from the few and in part untrustworthy observations, it appears that, from the maximum to the minimum of atomic volumes, the elements are entirely magnetic, and at the minimum the magnetism exhibits the greatest intensity; this is at least true of the iron group; then from this minimum to the next maximum follow diamagnetic elements only. The first period includes two atomic volume periods; this is remarkable, since by this means the elements N, O, F, Na, Mg, Al, and Si are separated from the elements resembling them, viz. P, S, Cl, and K, &c., and are associated with those with which they have but little in common.

This peculiar relationship cannot be attributed alone to the unreliable nature of the observations, inasmuch as the magnetic character of oxygen and the diamagnetic properties of the nearly associated elements S, Se, and Te have been established by accurate and trustworthy experiments. Hence it appears that, at least in this group, magnetic properties must be attributed to the element with small atomic weight which bears the least resemblance to the other members of the same group. Hence the magnetic character of an element is not determined by its atomic volume, but appears to be nearly related to its electro-chemical properties, and in such a way that every magnetic period embraces two periods of the electro-chemical; further, these may coincide with one and the same period of atomic volumes, or may extend over two.

Owing to the small intensity of the magnetic force of the majority of the elements, and the disturbing effect which a small amount of iron may produce, it would appear that although these speculations are not sufficiently reliable, yet they show the necessity for a renewed and complete investigation of the question.

§ 78. Although our knowledge of the interdependence between the physical properties and the atomic weight may still be incomplete, yet sufficient is known to show the necessity for the introduction of a new departure in physical investigation.

In physics hitherto place and time especially have been

regarded as the variable quantities upon which phenomena depend; further, under some circumstances heat, temperature, electricity, and some other quantities have been introduced into the calculation; the substance experimented with appeared in the calculations as mass only, expressed in weight and number. The quality of the substance was introduced into the differential equation or equation of conditions, as a constant varying with each species of matter. Formerly it was not customary to regard these magnitudes as variable, which are dependent upon the nature of the substances.

The intrinsic nature of matter has already received some consideration, as far as concerns its influence upon physical phenomena, since it has been customary to determine the physical constants of the most diverse substances. This intrinsic nature of matter always remained of a qualitative character, and it was not possible to introduce these fundamental variables, expressed in weight and number, into calculations. A beginning, although but primitive, has been made towards the true estimation of these variables. For it has been shown that the numbers representing the atomic weights are the variables by which the real nature of a substance, and the properties depending upon it, are determined. The atomic weight is therefore the new variable to be introduced into the calculations; the properties of matter or physical phenomena are no longer to be regarded as functions of place and time, &c., but as functions of the atomic weights. The mathematical form of this function still remains to be discovered; it will in all probability prove to be a very strange one. This function may be discontinuous, inasmuch as for certain cases of the argument only real values have been obtained, viz. for the atomic weights of the elements at present known. There is at present but little probability of expressing this relationship exactly; for the determinations of the atomic weights of some of the elements are so inexact that the error may in some cases amount to several per cent. of the whole.

The immediate object of investigation in this province will be to obtain empirically numbers exhibiting the interdependence between the properties and the intrinsic nature of the

elements and compounds. We may hope, however, that the positions already gained may prove a sufficient inducement to physicists to investigate thoroughly and systematically the physical properties of the elements and of their analogous compounds. The existence of such a comprehensive and comparable series of observations would, by the aid of suitable hypotheses, facilitate the attainment of a common standpoint for theoretical considerations.

§ 79. The numbers expressing the atomic weights form the only sure basis for a systematic arrangement of the elements and their compounds; further, this arrangement resembles that of organic compounds. The elements in the vertical series in the table on p. 120 form a natural family (which are styled 'groups' by Mendelejeff). The horizontal series represents an electro-chemical period, and forms what Mendelejeff styles a 'series.' The latter corresponds to the heterologous, the families or groups to the homologous series of organic compounds. Each family consists of two classes, the members of which are most easily distinguished from one another by their positions on the curve of atomic volumes. The term 'group' is, in order to prevent confusion, applied to the classes of these families.

The two groups of the first family are:

I.	*A.*	Li	Na	K	Rb	Cs	—	
	B.			Cu	Ag	—		Au

The members of the group *A* occur at the maxima of the curve of atomic volumes; whilst those of group *B* occur near the minima. These two groups differ considerably, but afford certain analogies, *e.g.* as regards the equivalent proportions, quantitative composition, and isomorphism of their compounds, Na exhibits isomorphism with members of the second group.[1]

The second family contains the following metals, the members of the first group occur on the descending and those of the second on the ascending curve:

II.	*A.*	Be	Mg	Ca	Sr	Ba	—	
	B.			Zn	Cd			Hg

[1] Mendelejeff places Na in the second group. For its magnetic relations, *vide* p. 151.

The contrast between these two groups is less striking than in the case of the first family; this is especially true of the elements zinc and magnesium.[1]

The first two members of the third and fourth families occur near the minimum of the curve of atomic volumes, whilst the other members occur partly on the descending and partly on the ascending portions of the curve. Consequently the first members of these families do not resemble the other members as closely as the members of the first family resemble one another; in fact, these first members resemble the elements of one of the groups only. The elements in the isolated state resemble those of one group, whilst their compounds to some extent resemble those of the elements of the other group. If special weight be attached to the behaviour of the elements themselves, and due consideration be given to the differences exhibited in the reducibility of their oxides, a property dependent upon their affinity for oxygen, then the first members of these families would be counted as members of the groups situated on the descending curves.[2] In this group of the third family, the case is rendered more complex, owing to the fact that instead of one element there are three which possess almost the same atomic weight, viz. lanthanum, cerium, and didymium. Their properties fully coincide with those of the members of this group, and if only one of the three was known we should unhesitatingly place it in this position. As the existence of these three elements is beyond dispute, although it is probable that not one of them has been obtained in a state of absolute purity, it appears advisable to treble this group, like group VIII., so as to make room for the numerous earthy metals which are supposed to have been, or in reality have been, recently discovered. This was done in the 4th edition of this book with the idea that further investigation of the newly discovered earth metals would fill the vacant spaces in this treble series. Contrary to expectation, it now appears probable that the list of the so-called

[1] In consideration of this fact, Mendelejeff has arranged this family as follows:

II.	*A.*	Be	Ca	Sr	Ba	—	
	B.		Mg	Zn	Cd	Ng	Hg

[2] Mendelejeff places Si and Al in other groups.

new earth metals will be reduced to a small number. In order to avoid the numerous empty spaces in the table, Brauner's [1] arrangement of these elements has been adopted in this edition, although his classification can only be regarded as a temporary arrangement. Although Brauner has shown that the oxides of cerium and didymium have the composition CeO_2 and Di_2O_5, this fact alone does not justify us in definitely classing these elements in groups IV. *A* and V. *A*. Although cerium resembles zirconium in many respects, there are few points of resemblance between didymium and niobium and tantalum. Its atomic volume is too high. Both elements are easily fusible and malleable, and differ from the other refractory and brittle members of groups IV. *A* and V. *A*.

Of course it is possible that the missing elements between cerium and tantalum, and between bismuth and thorium, may exhibit a greater difference in their properties from the members of the same class with lower atomic weights than these elements exhibit amongst themselves. At the present time we are scarcely in a position to determine whether the curve of atomic volumes will in this case be analogous to the former sections of the curve. The existence or non-existence of the doubtful earth metals must be decided before the position of the other earth metals can be finally determined. If we omit erbium, terbium, decipium, holmium, thulium, samarium, &c., we have the following groups:

III.	*A.*	B	Al	Sc	Y	La	Yb	—
	B.			Ga	In	—	Tl	
IV.	*A.*	C	Si	Ti	Zr	Ce	—	Th
	B.				Sn		Pb	

In the fifth, sixth, and seventh families the minority consists of difficultly fusible and difficultly reducible elements, occurring on the descending portions of the curve; the first members belong to the groups the members of which occur on the ascending portions of the curve. These families contain the following elements:

V.	*A.*			V	Nb	Di	Ta	—
	B.	N	P	As	Sb	—	Bi	

[1] *Chem. Soc. Jour. Trans.* 1882, 78.

VI.	*A.*			Cr	Mo	—	W	U
	B.	O	S	Se	Te	—	—	;
VII.	*A.*			Mn	—	—	—	—
	B.	F	Cl	Br	I	—	—	

The more abruptly the chemical character of the elements in the second group of these families developes with increasing atomic volumes, so much the more do the isolated elements of each group differ from one another, whilst, on the other hand, the resemblance in their compounds remains more marked. This fact is illustrated by chlorine and manganese in VII.

The eighth family consists of three groups, or rather, there are three groups arranged together, the members which would form a group corresponding to VII. *B* are, however, wanting. It is at present impossible to say whether such a group could exist, thus forming the link between the negative elements fluorine, chlorine, and the positive elements of the alkali group. Owing to the resemblance exhibited by the members of the eighth family, they are not divided into groups, but are placed in one family thus :

VIII. Fe Co Ni Ru Rh Pd Os Ir Pt

It is of no consequence whether we subdivide these groups, since they form a link between VII. *A* and I. *B*; a fact at once evident, if we consider the table of atomic weights on p. 120 as rolled on a vertical cylinder.

§ 80. An acquaintance with the relation of the atomic weights to one another, and to the properties of the elements, has served in many cases as a useful means of avoiding errors and of extending our knowledge.

By its aid we can determine pretty accurately the value of the coefficient n, mentioned in §§ 2 and 3, in those cases where neither the law of Avogadro nor that of Dulong and Petit can be applied.

According to Cl. Winkler,[1] 4·737 parts by weight of indium on oxidation, combine with one of oxygen, therefore

$$Q : Q_1 = 4{\cdot}737 : 1 = n\,In : n_1\,O$$

$$In = \frac{n^1}{n} 4{\cdot}737 \cdot 15{\cdot}96 = \frac{n^1}{n} 75{\cdot}6$$

[1] *Journ. f. prakt. Chem.* 1867, cii. 273.

Formerly it was supposed that $n = n^1$, hence In = 75·6 and In O = 75·6 + 15·96.

Mendelejeff[1] used this value for the atomic weight of indium in his first arrangement of the elements. But as with this atomic weight it would stand between arsenic and selenium, a position irreconcilable with its chemical nature and atomic volume, the author in a paper[2] on the properties of chemical elements as functions of their atomic weights, pointed out that if $n=2$ and $n_1 = 3$, then In = 113·4 and its oxide would have the formula In_2O_3. Indium would then stand between cadmium and tin, a position analogous to that of thallium, between mercury and lead. This supposition was shortly afterwards confirmed by Bunsen's[3] determination of the specific heat of indium.

Awdejew[4] found that 4·63 parts by weight of beryllium are equivalent to one part by weight of hydrogen. Nilson and Pettersson[5] found the corrected value to be 4·54. The atomic weight, therefore, Be = n 4.54, n being a small number, either 1, 2, or 3. Berzelius was led by the similarity exhibited by aluminium and beryllium to suppose that $n = 3$, hence the atomic weight is 13·6; Awdejew, on the other hand, took $n = 2$, and hence the atomic weight is 9·08. This last value is the only one which accords well with the system of atomic weights, for with the atomic weight 13·6 beryllium must be placed between carbon and nitrogen, a position ill-suited to an electro-positive metal. With the atomic weight 9·08 it must be placed immediately after lithium, a position in the series of atomic weights completely analogous to that of magnesium[6] and the other metals of the alkaline earths. Since this position was assigned to beryllium, Reynolds determined its specific heat, and found it to be in accordance with the atomic weight 9·08. Nilson and Pettersson, however, found its specific heat much smaller than it should be, supposing its

[1] *Zeitschr. f. Chem.* 1869, N.F. 405.

[2] *Lieb. Ann.* 1870, Suppl.-Bd. vii. 362. *Pogg. Ann.* 1870, cxli. 1.

[3] *Bull. der Petersb. Akad.* xvi. 45.

[4] *Ber. d. deut. chem. Ges.* 1880, 1451.

[5] Be resembles Mg in forming a sparingly soluble double salt with ammonium phosphate—Rössler, *Fres. Zeits.* 1878, xi. 148.

atomic weight to be 13·6. Brauner's [1] hypothesis that the specific heat of beryllium, like that of its neighbours boron and carbon, varies considerably with the temperature, has been confirmed by the investigation of Nilson and Pettersson, mentioned in § 38. Further, Carnelley [2] has shown that the melting points of the halogen compounds of beryllium are more in accord with the atomic weight Be = 9·08. Since the melting points would appear quite irregular if the formulæ $BeCl_3$, $BeBr_3$, &c. (Be = 13·6) are accepted; whereas with the formulæ $BeCl_2$, $BeBr_2$, &c. (Be = 9·08), the agreement is so great that Carnelley was enabled to calculate them accurately, before he had determined them by experiment. These reasons decide in favour of the atomic weight 9·08 for beryllium.

Mendelejeff, before the specific heats of cerium, lanthanum, and didymium were known, proposed that the atomic weights of the cerite and gadolinite metals should be increased by half their present value.

Similar conjectures have been made for other elements, which, although they have not led to accurate determinations of the atomic weight, yet they have shown the improbability of some determinations which had formerly passed uncontested. For instance, the author pointed out that in the case of uranium, none of the atomic weights U = 60 or U = 120 could be reconciled with the density of the metal 18·4. The value 180 was more probable, but this has become much less so, since Roscoe [3] has shown that with U = 120 the chloride discovered by him has the formula UCl_5 analogous to that of molybdenum $MoCl_5$. The atomic weight U = 240 was finally determined by Zimmermann's investigation (*vide* §§ 23 and 39).

The relations between the atomic weights and the properties of the elements, though useful, are still insufficient aids for the determinations of the atomic weights. It can be stated generally what atomic weights an element cannot have; but we can only make conjectures as to which is the

[1] *Ber. d. deut. chem. Ges.* 1878, 872.

[2] *Proc. Roy. Soc.* 1879, No. 197; *Phil. Mag.* [5] 1879, viii. 371; *Chem. Soc. Journ.* 1880, 126.

[3] *Ber. d. deut. chem. Ges.* 1874, 1131.

real atomic weight of an element. That this is the case, and that we cannot assign an atomic weight to an element from the determination of its equivalent alone, is shown by the fact that, based upon these relations, very different conclusions have been drawn as to the atomic weight of one and the same element. Thus, for example, Mendelejeff proposed, at two different periods, the following atomic weights:

1869	1871	1869	1871
Eb = 56	Eb = 178	La = 94	La = 180
Y = 60	Y = 88	Di = 95	Di = 138
In = 75·6	In = 113	Th = 118	Th = 231
Ce = 92	Ce = 140	U = 116	U = 240

The values proposed in 1869 have proved to be incorrect, as also has the atomic weight of lanthanum proposed in 1871.

§ 81. The regularities exhibited by the numbers representing the atomic weights have, moreover, led to a correction of stochiometric constants.

The atomic weight of caesium was found by Bunsen, who experimented with a very small quantity of this rare element, to be 123·4. This number disturbs the regularity observed in the differences between the atomic weights of the alkali metals thus:

Li = 7·01, Na = 22·99, K = 39·04, Rb = 85·2 (Cs = 123·4).
Differences 15·98 16·05 46·16 38·2

It was, therefore, to be expected that the atomic weight of caesium would be somewhat larger than 123·4, an expectation which the experiments of Johnson and Allen[1] have shown to be correct. These chemists found the atomic weight of caesium to be 132·7,[2] a number which was immediately confirmed by Bunsen.[3] By using this number the irregularities exhibited by the differences between the atomic weights of these metals disappear, thus:

Li = 7·01, Na = 22·99, K = 39·04, Rb = 85·2, Cs = 132·7
Differences 15·98 16·05 46·16 47·5

[1] *Sill. Amer. Journ.* [2] 1863, xxxv. 94.

[2] This number is calculated supposing Ag = 107·66 and Cl = 33·37, but taking the numbers used by Johnson and Allen, Ag = 107·94 and Cl = 35·46, then Cs = 133·0.

[3] *Pogg. Ann.* 1863, cxix. 1.

According to the relations between the atomic weights of the elements given in §§ 61 and 64, it is probable that

$$Os < Ir < Pt < Au,$$

whilst the older determinations give

$$Os > Ir = Pt > Au,$$

thus showing the necessity for new atomic weight determinations for these elements. In fact, K. Seubert[1] concludes that Ir < Pt and Pt < Au,[2] and J. Thomsen[3] has detailed experiments which show that the accepted atomic weight of gold (Au = 196·2) is too small.[4] Proof is still wanting in the case of osmium; and although the atomic weight of Os = 198·6 is some six units too large, yet it would not be permissible to alter the atomic weight so as to accord with the system, unless new quantitative determinations of the atomic weights showed such a change to be required.

From the analogy with its associates, tellurium should come before iodine in the series of atomic weights. The atomic weight of tellurium has been redetermined by W. L. Wills,[5] and Te = 127·8 is given as the mean of the majority of the analyses. This number is larger than the value which Stas was led, from very exact determinations, to assign to iodine, viz. I = 126·53. But since the mean of some of the analyses, although differing considerably from the others, yet agreeing well amongst themselves, give the atomic weight of tellurium Te = 126·3, this number may be employed until further experiments have been made.

§ 82. In cases where the atomic weights as determined by several investigators or by different methods differ considerably, it is often possible to distinguish between the correct and incorrect results.

[1] Inaug. Diss. Tübingen, 1878; *Ber. d. deut. chem. Ges.* 1878, 1767.

[2] *Lieb. Ann.* 1880. ccvii. 29.

[3] *Journ. f. prakt. Chem.* 1876, N.F. xiii. 346.

[4] Krüss (*Ber. d. deut. chem. Ges.* Feb. 1887) gives as the results of his determinations the atomic weight 196·64 for gold, whilst Thorpe and Laurie, in a paper communicated to the Chemical Society, April 1887, assign to this element the atomic weight 196·85 as the mean of their experimental results.

[5] *Chem. Soc. Journ.* 1879, 704.

The atomic weight of molybdenum has, according to some investigators, been found to be 96, and by others to be 92 (in round numbers). There was but little probability in favour of the correctness of this latter determination, for then molybdenum must be placed in an entirely false position in the system of atomic weights, viz. before niobium. The more recent experiments of Liechti and Kempe[1] have, in fact, shown the error of this last atomic weight determination.

An examination of the atomic weights of the following groups of elements

	Difference		Difference	
Fe = 55·9	47·6	Ru = 103·5	95·1	Os = 198·6
Co = 58·6	45·5	Rh = 104·1	88·6	Ir = 192·7
Ni = 58·6	47·6	Pd = 106·2	88·1	Pt = 194·3
Cu = 63·2	44·5	Ag = 107·7	88·5	Au = 196·2
Zn = 64·9	46·8	Cd = 111·7	88·1	Hg = 199·8
Ga = 69·9	43·5	In = 113·4	90·3	Tl = 203·7
—	—	Sn = 117·4	89·0	Pb = 206·4
As = 74·9	47·1	Sb = 122·0	88·0	Bi = 210·0
—	45·1	Sb = 120·0	87·5	Bi = 207·5

shows the differences between the atomic weights of their members to be approximately the same. In the case of osmium, however, its atomic weight appears to be some six or seven units too large, whilst that of indium appears about two units too small. No conclusion can be drawn as to whether the atomic weight of antimony is 120, as found by Schneider[2] and confirmed by Cooke,[3] or whether it is 122, as found by Dexter[4] and confirmed by Kessler.[5] Although the difference between the atomic weights of arsenic and antimony is 47 when the number 122 is accepted, yet the latest determinations of Cooke[6] show that the number 120 is to be

[1] *Lieb. Ann.* 1873, clxix. 360.

[2] *Pogg. Ann.* xcvii. 483; xcviii. 293; *Ann. Chem. Pharm.* c. 120.

[3] *Proc. of the Amer. Acad. of Arts and Science*, xii. 1; *Sill. Journ.* [3] xv 41, 107; *Ber. d. deut. chem. Ges.* 1878, 255.

[4] *Pogg. Ann.* c. 570.

[5] *Ibid.* cxiii. 145; *Das Atomgewicht des Antimons*, Bochum, 1879.

[6] *Proc. Amer. Acad.* March 10, 1880, 251.

preferred. It may, however, be safely asserted that should Schneider's number prove to be correct, then his determination of the atomic weight of bismuth, viz. Bi = 207·5,[1] is probably correct, whilst Dexter's atomic weight of antimony is only adapted to Dumas'[2] atomic weight of bismuth, viz. Bi = 210.

The relations of the differences between atomic weights justify us in making a selection from different experimental results; still our knowledge is too uncertain to allow of theoretical adjustments of numbers obtained by experiments. There can be no doubt as to the fact that these differences are subject to law. When the small deviations in the values obtained for these differences are disregarded, the matter appears more simple than it in reality is. For instance, if for the elements with small atomic weights suitable round numbers are used, a general difference of 16 is obtained, thus:

						Li = 7	Be = 8
Difference	—	—	—	—	—	16	16
	B = 11	C = 12	N = 14	O = 16	F = 19	Na = 23	Mg = 24
Difference	16	16	16	16	16	16	16
	Al = 27	Si = 28	P = 30	S = 32	Cl = 35	K = 39	Ca = 40

But the atomic weights which are used to attain such a regularity differ considerably from the values obtained by experiment. To some extent these deviations may be regarded as arising from errors in the determinations of the atomic weights. That this cannot be asserted of all has appeared probable for some time, but the investigations of Stas have placed this beyond question. Liebig's[3] remarks, made some years ago on Prout's hypothesis, are applicable in this case also. The values of the numbers and their relations 'are stated as facts; the law upon which these numbers are based is, however, unknown to us.' Hence chemists, in order to exhibit some possible connection, have never been, and are certainly not at present justified in

[1] *Pogg. Ann.* lxxxii. 303; *Lieb. Ann.* lxxx. 204.
[2] *Ann. Chim. Phys.* [3] 1859, lv. 177.
[3] *Lieb. Ann.* 1853, lxxxv. 256.

making arbitrary changes and corrections in the atomic weights obtained empirically. Such changes have been too frequently proposed, but can only be justified when based upon more exact experimental evidence.

§ 83. Speculations upon the existence and properties of the elements required to fill the blanks occurring in the systematic arrangements of the elements according to their atomic weights although attractive are inconclusive. Such blank spaces are found in many of the series given in the table in § 61; their number was at first much larger; the corrections in the atomic weights described in the foregoing paragraphs, have served, by assigning elements to them, to lessen this number.

Mendelejeff[1] has gone a step further, and has been able to draw many happy conclusions regarding the properties of the still undiscovered elements, which will fill up some of these blank spaces.

The possibility of so doing is based on the conception that the properties of the elements in the series, and also in the groups, vary in a more or less continuous manner, although to different extents. In many cases the resemblance is greater amongst the members of the groups than amongst those of the series; for example, there is a greater similarity between Ca, Sr, and Ba than between Rb, Sr, and Y. In other cases the reverse holds good, a greater resemblance being exhibited by the members of the series Mn, Fe, Co, and Ni than by the members of either of the groups Fe, Ru, Os, or Co, Rh, and Ir, &c. The properties of an element are, as a rule, the means of those of its neighbours in the groups on the one hand, and of the series on the other. Mendelejeff[2] styles these four elements so related, 'atomic analogues.' The 'atomic analogues' of selenium are, on the one hand, sulphur and tellurium; arsenic and bromine on the other. The relations between their densities, atomic weights, and atomic volumes are exhibited in the following table, and they exhibit similar relations in their other properties.

[1] *Lieb. Ann.* 1871; Suppl. viii. 196.
[2] *Loc. cit* 165

Density			Atomic Weight			Atomic Volume		
	S 2·04			S 31·98			S 15·7	
As 5·67	Se 4·6	Br 2·97	As 74·9	Se 78·87	Br 79·76	As 13·2	Se 17·2	Br 26·9
	Te 6·25			Te 126·3			Te 20·2	

By similar considerations Mendelejeff was led to predict the properties of the element situated between boron and yttrium, to which he gave the name 'ekaboron,' and also those of the element between aluminium and indium, which he styled 'eka-aluminium.' Some of the properties ascribed to eka-aluminium were found to correspond with those of the element gallium, discovered later on by Lecoq de Boisbaudran. This led Mendelejeff to predict that not only would the atomic weight of gallium be 68, but that its properties would correspond with those of the element 'eka-aluminium.' This prediction has, in all important respects, proved to be correct, even in regard to those points to which the first observations of the discoverer were apparently opposed. For instance, the discoverer first attributed the density 4·7 to this element, but according to Mendelejeff's prediction, the density should have been 5·9; a new determination with purer material confirmed the correctness of this prediction—the density was, in fact, found to be 5·96.

Nilson[1] discovered scandium, and on the ground of a preliminary investigation, made with three decigrams of impure oxide containing ytterbium, he regarded Sc as a tetravalent metal, having an atomic weight of about 170. Cleve,[2] however, pointed out that the true atomic weight of Sc is 45 and that the metal is identical in all its properties with ekaboron. This result was afterwards confirmed by Nilson,[3] who found the atomic weight of pure scandium to be 44.

It is much easier to make conjectures as to the unknown properties of known elements. Before the density and melting point of caesium were determined, these properties were given in the table of atomic volumes and melting points almost

[1] *Ber. d. deut. chem. Ges.* 1879, xii. 554. [2] *Compt. rend.* 1879, lxxxix. 419.
[3] *Ber. d. deut. chem. Ges.* 1880, xiii. 1441.

exactly as found by Setterberg. The specific heat of caesium, $c = 0{\cdot}05$, could also be predicted with certainty.

The prediction of the properties of undiscovered elements is one of the most attractive, but also most difficult, problems of the science of chemistry. It resembles to some extent the prediction, so astonishing to the uninitiated, of undiscovered planets. Although the problem is not dissimilar to that presented to the astronomer, yet it must not be forgotten that the aids afforded by chemistry for its solution are much weaker and less reliable than those of astronomy, which depend on the dynamical principle of Newton's law of gravitation.

But although convinced of the fallibility of our methods, yet it is always permissible to test them by predicting, as accurately as possible, the properties of still undiscovered elements; so that we may afterwards compare them with the results of observation, and hence form some conception of the value of such theoretical speculations.

§ 84. The laws relating to the atomic analogues are not general, inasmuch as the first members of the entire series, as far as and including silicon, exhibit an entirely different periodicity. Hence, for example, nitrogen can scarcely be regarded as the analogue of vanadium, or oxygen as that of chromium. The elements with small atomic weights, from hydrogen to silicon, form a series of what Mendelejeff styles typical elements, and may be regarded as types of the others. Mendelejeff does not consider aluminium and silicon as belonging to these elements, although the great differences between them and the easily fusible and easily reducible members of the corresponding groups—viz. Ga, In, Tl, and —Sn, Pb—necessitate such a classification. These large periods commence with phosphorus, in which elements similarly situated exhibit complete analogies. This is shown in the following table:

Types			Li	Be	B	C	N	O	F				Na	Mg	Al	Si
P	S	Cl	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	—
As	Se	Br	Rb	Sr	Y	Zr	Nb	Mo	—	Ru	Rh	Pd	Ag	Cd	In	Sn
Sb	Te	I	Cs	Ba	La	Ce	Di	—	—	—	—	—	—	—	—	—
—	—	—	—	—	Yb	—	Ta	W	—	Os	Ir	Pt	Au	Hg	Tl	Pb
Bi	—	—	—	—	—	Th	—	U								

The typical elements following nitrogen exhibit but little analogy with the groups placed below them; the analogy is, however, somewhat more striking after magnesium. Hence the following arrangement would also appear to be justifiable:

			Li	Be	B	C									
N	O	F	Na	Mg	Al	Si									
P	S	Cl	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	—
As	Se	Br	Rb	Sr	Y	Zr	Nb	Mo	—	Ru	Rh	Pd	Ag	Cd	In	Sn
Sb	Te	I	Cs	Ba	La	Ce	Di	—	—	—	—	—	—	—	—	—
—	—	—	—	—	Yb	—	Ta	W	—	Os	Ir	Pt	Au	Hg	Tl	Pb
Bi	—	—	—	—	—	Th	—	U								

As early as 1869 Mendelejeff[1] pointed out that the elements regarded as typical are widely distributed in nature, as are also those in their immediate proximity, as far as calcium. Of all the other elements there is only iron, and perhaps manganese and arsenic, which occur in quantities approaching the others. This occurrence is possibly a consequence of the smallness of their atomic weights; nevertheless, it is remarkable that three elements—Li, Be, and B—with the smallest atomic weights next to hydrogen belong to the rare elements.

§ 85. Mendelejeff[2] represents the relations described in the above paragraphs somewhat differently. The table on the next page illustrates his arrangement of the elements.

In this table the families are denoted by Roman numbers, and the series by Arabic. According to Mendelejeff, the elements occurring in the uneven series may be distinguished from those in the even ones by certain characteristic properties. The characteristic properties which Mendelejeff gave do not always meet the case. For instance, he states 'that the members of the even series possess the basic character, whilst the corresponding elements in the uneven series have more of the acid nature.' He soon discovered that this is not generally true, and, in order to lessen the exceptional cases, Cu, Ag, Au are surrounded by brackets in the first group, and then placed in group VIII. in the even series. But even with this the

[1] *Zeitschr. f. Chemie*, N.F. 1869, v. 405.
[2] *Lieb. Ann.* 1871; Suppl. viii. 151.

electro-positive elements remain in exceptional positions; thus Na, Mg, Zn, Cd, Hg, Al, In, Tl, and Pb remain as positive and, in part, as strongly positive elements. A consideration of the matter, unfettered by preconceived notions, shows that as many positive as negative elements occur in the even series, namely, twelve of each kind. It is easy to

MENDELEJEFF'S TABLE.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.			
1	H 1										
2	Li 7	Be 9·4	B 11	C 12	N 14	O 16	F 19				
3	Na 23	Mg 24	Al 27·3	Si 28	P 31	S 32	Cl 35·5				
4	K 39	Ca 40	Sc 44	Ti 48	V 51	Cr 52	Mn 55	Fe 56	Co 59	Ni 59	Cu 63
5	(Cu) 63	Zn 65	Ga 69	— 72	As 75	Se 78	Br 80				
6	Rb 85	Sr 87	? Y 88	Zr 90	Nb 94	Mo 96	— 100	Ru 104	Rh 104	Pd 106	Ag 108
7	(Ag) 108	Cd 112	In 113	Sn 118	Sb 122	Te 125	I 127				
8	Cs 133	Ba 137	? Di 138	? Ce 140	—	—	—	—	—	—	—
9	(—)	—	—	—	—	—	—				
10	—	—	? Er 178	? La [1] 180	Ta 182	W 184	—	Os 195	Ir 197	Pt 198	Au 199
11	(Au) 199	Hg 200	Tl 204	Pb 207	Bi 208	—	—				
12	—	—	—	Th 231	—	U 240	—	—	—	—	—

understand that such a division of the elements into twelve series is arbitrary. A comparison with the table in § 61 shows that a line may be drawn before or behind any group, and

[1] An assumption not confirmed by experiment.

still series analogously constituted are obtained; so, for example—

Li,	Be,	B,	C,	N,	O,	F	Na,	Mg,	Al,	Si,	P,	S,	Cl	&c.
or Be,	B,	C,	N,	O,	F,	Na	Mg,	Al,	Si,	P,	S,	Cl,	K	,,
,, B,	C,	N,	O,	F,	Na,	Mg	Al,	Si,	P,	S,	Cl,	K,	Ca	,,
,, C,	N,	O,	F,	Na,	Mg,	Al	Si,	P,	S,	Cl,	K,	Ca,	—	,,
,, N,	O,	F,	Na,	Mg,	Al,	Si	P,	S,	Cl,	K,	Ca,	—	Ti	

and so on.

Each series will, divide it as you may, always contain elements which are positive and negative, malleable and brittle, difficultly fusible and easily fusible and volatile. From the explanations already given it is seen that this cannot be otherwise.

§ 86. In all these speculations we must not lose sight of the fact that the general law upon which the relations between the properties of an element and its atomic weight depend is still unknown. There are many of the groups of elements formed by the systematic arrangement of the atomic weights the properties of the members of which would scarcely warrant their classification as a natural family, had not the relations of the numbers expressing their atomic weights indicated the necessity for such a classification. To whom would it ever occur to regard boron and thallium, oxygen and chromium, or fluorine and manganese, as members of the same group? Silver has frequently been placed amongst the alkali metals, but gold and copper have never hitherto been associated with them. In fact, the position of these metals, including silver, has been so much a matter of doubt that formerly they were not placed in the atomic weight series, but were placed at the end of this series—a position indicating our uncertainty with regard to these elements. The uncertainty of our knowledge is also shown by the different results obtained when attempts have been made to classify the elements by means of any other properties save the fixed numerical values of their atomic weights.[1]

There can no longer be any doubt that the system of the

[1] This is well illustrated by the repeated changes in the position of the elements in Mendelejeff's various papers on the subject; also by the tortuous lines on Baumhauer's spiral table.

elements based upon the values of their atomic weights will form the basis of future doctrines of comparative affinity. Still the advances made hitherto do not suffice for the foundation of this theory deductively from one or a few general principles. We must advance by the aid of induction and with special care, steadily remembering the words of Bacon: 'Gestit enim mens exsilire ad magis generalia, ut acquiescat, et post parvam moram fastidit experientiam.'[1] Hence the natural tendency to generalise must be kept in check as much as possible, and we must still depend upon experimental observations for our advance in this unexplored province. Hypotheses may certainly be used to aid our progress, but only when these are carefully distinguished from the results of observation; for if we are to reap the expected fruit from such a rich field, free from the tares of error, then care must be taken not to confuse theory and observation. This progress will necessitate quite a new series of observations, old observations must be confirmed, and in some cases corrected, and many new ones made. There is still much work for the hands and mind; but it will be thoroughly rewarded. The prize is a systematic inorganic chemistry which will not fear comparison with the thoroughly developed system of organic chemistry.

[1] *Nov. Org.* I. Aphor. xx.

PART II.

STATICS OF THE ATOMS.

VI.

FORMS OF COMBINATION. TYPES.

§ 87. The value and the importance of the two hypotheses which are especially used for determining atomic weights, viz. Avogadro's and Dulong and Petit's, can only be thoroughly appreciated when these atomic weights are employed to represent the composition of chemical compounds. The statement which Laurent[1] justly made concerning the atomic weights deduced from Avogadro's law alone, is still more applicable to the atomic weights deduced by the aid of both hypotheses. If the composition of chemical compounds is expressed by means of these atomic weights, 'we then obtain those chemical formulæ which exhibit the greatest simplicity, best indicate the analogies between different substances, agree best with the regularities in their boiling points and with isomorphism, and most clearly explain the chemical changes of bodies; in short, thoroughly fulfil all the requirements of chemists.'

Avogadro's hypothesis in particular has exerted a great influence on the development of chemical theories. It was only after it had been received and put into practice that the most important of those laws which govern the union of the atoms to form compounds were acknowledged.

The commencement of a general chemical theory has arisen from Avogadro's ideas. This theory endeavours to explain the atomic constitution of compounds and many of their properties by the peculiar and invariable forces and properties dwelling in the individual atoms, which are characteristic of the different elements.

[1] Laurent, *Méthode de Chimie*, 89.

The first development of this theory is the commencement of a doctrine of the equilibrium of the atoms, marking a new epoch in the history of chemical statics.

Having already considered the means which led to a logical and accurate determination of the weight and properties of the atoms, we can now turn to a description of the beginning which has been made in the statics of the atoms.

The relative masses of the atoms, the atomic weights determined by the methods already described, form the basis of the statics of the atoms. They are the invariable values, the constants of the theory.

§ 88. In order to recognise the general laws which govern the union of the atoms to form compounds, it is in the first place necessary to learn the composition of a molecule of each compound, or, in other words, the composition of the smallest particles of each substance which cannot be further divided without changing the nature of the substance. The determination of the weight of these groups of atoms called molecules is accomplished with a degree of probability approaching certainty, in the case of gaseous compounds, by means of Avogadro's hypothesis, that under the same pressure and temperature equal volumes of all gases contain the same number of molecules, and consequently the molecular weight is proportional to the density. ($\mathfrak{M} = 28{\cdot}87.\, d$, see § 16.)

The building up of an expression composed of atomic symbols for the composition of the molecule of a chemical compound is by no means new, being as old as the atomic theory itself. It has come into general use since the introduction of Berzelius' atomic symbols, which have replaced the less convenient symbols of Dalton. But a very different signification has been attached to these expressions of the composition, the formulæ of chemical compounds, not only at different times, but even at the same time by different chemists.

These changes in definition are exceedingly interesting and instructive, not only to the historian of chemistry, but also to the student of the spirit of investigation in man. They offer an excellent example of the endeavours of this spirit, which often sets itself lofty problems and works actively at their

solution, then almost despairing of the possibility of their solution, finally, after repeated endeavours, approaches nearly to the goal which at first appeared so distant.

Since Dalton's time two essentially different ideas have been opposed to each other. One declares that not only the knowledge of the building up of the molecules from atoms, but also the discovery of the manner in which these atoms are united to form a molecule, is a problem which can be solved by investigation, the other view regards the investigation of these matters as vain and fruitless, and uses chemical formulæ merely as an expression of the proportions by weight of the constituents of a compound as found by analysis. The supporters of the first view intend to represent by the symbols of Berzelius the really existing atoms, and to express by chemical formulæ how many of these atoms combine to form a molecule of the compound. The symbol H is used by them as the expression of a real value for an atom of hydrogen, O for an atom of oxygen, and the formula H_2O denotes that a particle or molecule of water consists of two atoms of hydrogen and one atom of oxygen. The results of recent investigations have silenced or converted the cautious opponents of these bold views. They doubted or disputed the possibility of gaining a glimpse at the constitution of compounds, and they regarded the chemical symbols not as representing the atoms, but merely as representing empirical stochiometric quantities. It is a matter of indifference to them whether the composition of water is represented by H_2O or HO. The empirical result of analysis, according to which water contains 7·98 parts of oxygen to one part by weight of hydrogen, can be equally well represented by either formula; only in the first case O must represent a quantity of oxygen which is 15·96, *i.e.* $2 \times 7{\cdot}98$ times as great as the amount of hydrogen, which is represented by H, whilst the second formula requires that $H : O = 1 : 7{\cdot}98$.

These two views were not always directly opposed, the opposition between them has always been toned down to a certain extent by the existence of less extreme ideas. This contrast was most marked during the twenty years' discussion which led to the adoption of the present system of organic

chemistry, which is essentially that proposed by Gerhardt. The defenders of this system have shown the full value of Avogadro's hypothesis and have prepared the way for the recent investigation of the laws which govern and determine the union of the atoms to form molecules. They were at first the declared opponents of the supposition that it is possible to recognise the mutual relation of the atoms in the molecule. But after their opposition had overthrown the views which formerly prevailed on this subject, they rapidly and successfully began to rebuild on the ruins of the structure they had overthrown. They now exchanged sides, and beginning to investigate the laws of atomic linking left the opponents of Gerhardt's system to dispute the new doctrines.

§ 89. It is only natural that in such a sudden change between defence and attack, assertion and denial, many confused and contradictory statements escaped notice which delayed although they did not stay progress. We are even at the present time not quite free from these contradictions, as may be seen on comparing a large number of the definitions contained in textbooks and theoretical treatises. The old contrast is still met with between a chemical formula which is intended to express the composition of a really existing particle and a formula which merely represents the relative quantities of the constituents of a stochiometric quantity. There is no harm in such a distinction. But the difference which is often made between 'physical' and 'chemical' molecules is ill-defined and therefore reprehensible.

In the attempt to determine the magnitude of the particles, the molecular weight, some investigators made use of certain physical properties, others considered the chemical behaviour of the substances. Both methods often led to the same result, to the same idea of the weight of the molecule, but also frequently to contradictory views and conclusions concerning molecular weights. It is in many cases difficult to state with certainty which of the values for the molecular weight, determined by the different methods is the correct one. But it is obvious that only one of them can be correct. Only two cases are possible, the substance in question either consists of distinct particles or molecules of a definite size, or it forms

a continuous system of particles not having separate subdivisions, in which case it is incorrect to speak of the size and weight of the molecules.

If the substance is really composed of distinct particles of matter, then these particles must be either identical with the smallest stochiometric quantities, which can be expressed by a chemical formula without making use of fractions of atoms, or they are rational multiples of this quantity. In the latter case it ought not to be called a particle of matter or 'molecule,' since it is only a fraction of a molecule. To define such a quantity as 'the smallest quantity of a substance which takes part in a chemical reaction' is quite inadmissible (see § 11), since less than a whole real particle cannot enter into a reaction with others.

For example, according to Avogadro's hypothesis, the molecular weight of arsenious anhydride is represented by the formula $As_4O_6 = 395{\cdot}4$, since Mitscherlich found the vapour density of this substance to be $13{\cdot}85$: $(13{\cdot}85 \times 28{\cdot}87 = 400)$. But half this molecular weight, viz. the quantity represented by the formula As_2O_3, is often used in equations representing chemical reactions.

This is permissible if it is clearly understood that this stochiometric quantity, which is the smallest which can be expressed by a formula, does not represent an actually existing isolated unit of matter, a so-called chemical molecule. A molecule cannot be either only 'chemical' or only 'physical,' but it must be either both at once or neither, *i.e.* it is really a molecule, or it is not.

So far all our experience has shown that the molecular weights deduced from Avogadro's hypothesis thoroughly correspond to the chemical and physical properties of the substances, so that by accepting these molecular weights all chemical reactions can be explained clearly and well, and much better and more simply than by any other assumption.

§ 90. Since Avogadro's law can only be applied to gaseous bodies, it is only in the case of such substances that a firm basis exists for determining the molecular weight, and for investigating the laws which govern the grouping together of

atoms to form molecules. We therefore confine ourselves at first to the consideration of gaseous bodies.

The previously defined unit is retained, the mass of a molecule of hydrogen gas is taken as $\mathfrak{H} = 2 = 2H$,[1] and the molecular weights of all other bodies as deduced from Avogadro's hypothesis are expressed by the usual symbols for the atoms composing the molecule. Or, to make use of the technical expression, molecular formulæ represent that quantity of each substance which occupies in the gaseous state the same volume as two parts by weight of hydrogen gas.

The table on the next page contains the molecular formulæ of all those compounds known to exist in the gaseous state, which are composed of two different elements, containing only a single atom of one of these elements in the molecule. The compounds are divided into six groups.

Column I. gives the name, II. the formula, III. the molecular weight $\mathfrak{M}$ expressed by the formula, *i.e.* the sum of all the atomic weights which occur in the formula; column IV. the density calculated from the molecular weight by means of the equation $28{\cdot}87 \,.\, d = \mathfrak{M}$; V. the observed density compared with atmospheric air as unity.

These six groups are distinguished from each other at the first glance by the fact that in the first group one atom of one element unites with only a single atom of the other constituent, whilst in the second group it unites with two, in the third with three, in the fourth with four, in the fifth with five, and finally in the sixth group with six atoms of the other constituent. The union of more than six atoms of one element

[1] Instead of this unit of mass A. W. Hofmann has proposed the weight of a litre of hydrogen gas measured at 0° C and 760 mm. pressure, which he calls a crith, as the unit (*Introduction to Modern Chemistry*, 1865, p. 131). The adoption of this unit cannot be recommended, since it gives rise to the idea that the values of the molecular weights are dependent on our units of weight and measure, whereas they are obviously perfectly independent of them so long as it is only the relative and not the absolute weight of the molecule which is determined. But if it should ever be possible to determine its absolute weight, a much smaller unit than Hofmann's crith would be required. The crith also has the disadvantage of varying with the geographical latitude; since the pressure of a column of mercury 760 mm. high increases with the increase in the intensity of gravity at the place of observation. Consequently a crith contains less matter in the tropics than in northern or southern latitudes.

TABLE OF VAPOUR DENSITIES.

I.	II.	III. M	IV. *d* calc.	V. *d* obs.
I.				
Hydrofluoric acid	HF	20·1	0·696 [1]	—
Hydrochloric acid	HCl	36·37	1·260	1·247
Hydrobromic acid	HBr	80·76	2·798	2·71
Hydriodic acid	HI	127·53	4·417	4·443
Iodine monochloride	ICl	161·9	5·61 [2]	—
Mercurous chloride	HgCl	235·2	8·130	8·35
Mercurous bromide	HgBr	279·6	9·685	10·14
Thallous chloride	TlCl	239·0	8·277	8·2
II.				
Water	OH_2	17·96	0·622	0·623
Chlorine monoxide	OCl_2	86·70	3·003 [1]	—
Sulphuretted hydrogen	SH_2	33·98	1·177	1·191
Seleniuretted hydrogen	SeH_2	80·9	2·802 [1]	—
Telluretted hydrogen	TeH_2	128·3	4·444	—
Cadmium bromide	$CdBr_2$	271·1	9·393	9·25
Lead chloride	$PbCl_2$	277·1	9·601	9·5
Mercuric chloride	$HgCl_2$	270·5	9·372	9·8
Mercuric bromide	$HgBr_2$	359·3	12·45	12·16
Mercuric iodide	HgI_2	452·9	15·69	16·2
III.				
Boron fluoride	BF_3	68·1	2·366	2·31
Boron chloride	BCl_3	117·0	4·057	4·02
Boron bromide	BBr_3	250·2	8·664	8·78
Ammonia	NH_3	17·01	0·589	0·597
Phosphine	PH_3	33·96	1·177	1·18
Phosphorous chloride	PCl_3	137·07	4·747	4·88
Arseniuretted hydrogen	AsH_3	77·9	2·699	2·695
Arsenious chloride	$AsCl_3$	181·0	6·270	6·30
Arsenious iodide	AsI_3	454·5	15·75	16·1
Antimony chloride	$SbCl_3$	225·7	7·82	7·8
Bismuth chloride	$BiCl_3$	313·6	10·86	11·35
IV.				
Marsh gas	CH_4	15·97	0·579	0·557
Carbon tetrachloride	CCl_4	153·45	5·315	5·33
Silicon fluoride	$SiFl_4$	104·4	3·616	3·57
Silicon chloride	$SiCl_4$	169·5	5·872	5·94
Silicon iodide	SiI_4	534·1	18·50	19·1
Titanium chloride	$TiCl_4$	189·5	6·566	6·84
Vanadium chloride	VCl_4	192·7	6·676	6·69
Zirconium chloride	$ZrCl_4$	231·5	8·019	8·15
Stannic chloride	$SnCl_4$	258·9	8·966	9·20
V.				
Phosphorus fluoride	PF_5	126·3	4·38	—
Niobium chloride	$NbCl_5$	270·8	9·383	9·4
Molybdenum chloride	$MoCl_5$	272·4	9·426	9·46
Tantalum chloride	$TaCl_5$	358·8	12·43	12·9
Tungsten chloride	$WoCl_5$	360·9	12·48	12·7
VI.				
Tungsten chloride	$WoCl_6$	396·2	13·73	13·2

[1] Indirectly determined. See §§ 20 and 23, note 1, p. 37.

[2] Meliköff's observations prove the correctness of this value for the density, which has been indirectly determined. (*Ber. d. deut. chem. Ges.* 1875, 480.)

with a single atom of another has not been observed with certainty in compounds capable of existing in the gaseous state and containing only two constituents.

The only compounds of two elements containing but a single atom of one of the constituents (the vapour density and molecular weight of which have been determined) which are not represented in the above table, are arranged below.

I.	II.	III. M	IV. *d* calc.	V. *d* obs.
I.				
Carbon monoxide . .	CO	27·93	0·968	0·968
Nitric oxide . . .	NO	29·97	1·039	1·039
II.				
Nitrogen peroxide . .	NO_2	45·93	1·591	1·59
Nitrous oxide . . .	ON_2	43·98	1·524	1·520
Sulphur dioxide . . .	SO_2	63·90	2·214	2·247
Selenium dioxide . .	SeO_2	109·9	3·807	4·03
Chlorine peroxide . .	ClO_2	67·29	2·331	—
Carbon dioxide . . .	CO_2	43·89	1·521	1·529
Carbon bisulphide . .	CS_2	75·93	2·630	2·645
III.				
Sulphur trioxide . . .	SO_3	79·86	2·766	3·01
IV.				
Osmic anhydride . .	OsO_4	262·4	9·090	8·9

These compounds will not at present be taken into consideration for reasons to be mentioned later on in § 96, and our attention will be confined to the six groups in the first table.

These six groups embrace the six simplest combinations of atoms, viz. of 1 atom with 1, 1 with 2, 1 with 3, 1 with 4, 1 with 5, and 1 with 6 others.

The three first of these combinations form, under the name of types, the basis of Gerhardt's so-called system of types, as presented in his treatise. It is to this system that the science of chemistry essentially owes its present form. Gerhardt named these three types after certain of their representatives; the first he called the hydrochloric acid, or hydrogen type (according to Avogadro's hypothesis, the molecule of hydrogen, HH, represents a combination of 1 : 1); the

second he called the water (or sulphuretted hydrogen) type; the third the ammonia type. In 1857 Kekulé [1] showed that a fourth type must be added, representing the combination 1:4; this is known as the marsh gas type.

The fifth type, to which at present no specific name has been affixed, is rendered necessary by recent investigations on niobium, tantalum, molybdenum, and tungsten, which show that the chlorides of these metals, which volatilise without decomposition, contain five atoms of chlorine in the molecule; the sixth type has been rendered necessary by the proof which Roscoe [2] has given, that tungsten hexachloride can exist in the gaseous state.

§ 91. The formation of these types, and the classification of all chemical compounds with them as models, has become of the utmost importance, since it is the expression of certain real and fundamental properties of matter which appear, more than all others, to govern and determine the constitution of chemical compounds. This attempt of Gerhardt was the commencement of the solution of the problem of which Laurent [3] said, 'Etablir une théorie des types, c'est établir une classification chimique basée sur le nombre, la nature, les fonctions et l'arrangement tant des atomes simples que des atomes composés.' The first laws of atomic statics have already arisen out of Gerhardt's system.

A cursory glance at the six groups of compounds suffices to show that many elements occur only in a single group, others in two, whilst some occur under almost all the types. But it is remarkable that the elements which occur in multiples in these compounds, and which determine the types by their number, are the same in almost every case, viz. in the first table, H, Fl, Cl, Br, and I; in the second, O, S, and N. It appears as though the atoms of these elements only had the power of uniting in large number with a single atom of another element. The five elements first mentioned, hydrogen, fluorine, chlorine, bromine, and iodine, are peculiar, inasmuch

[1] 'Ueber die sogenannten gepaarten Verbindungen und die Theorie der mehratomigen Radicalen,' *Ann. Chem. Pharm.* civ. 129.

[2] *Ann. Chem. Pharm.* 1872, clxii. 354.

[3] *Méthode de Chimie*, 358.

as they only form with each other gaseous compounds belonging to the first type.

The elements themselves, in the so-called isolated state, also belong to this type; as has been already pointed out their molecules consist of two atoms, HH, ClCl, II, and probably FF. In chemical reactions between these substances, each molecule is invariably halved, and only compounds of the first type are formed; *e.g.*

HH	+	ClCl	=	HCl + HCl
Hydrogen (1 mol.)		Chlorine (1 mol.)		Hydrochloric acid (2 mols.)

The hydrochloric acid resulting from the union of chlorine and hydrogen is unable to combine with more chlorine or hydrogen; it exerts no chemical action on these elements. The same holds good for all other compounds of the first type. A third atom of one of these elements cannot enter into the molecule unless it expels one of the two atoms which are already present. A union of three or more atoms to form a molecule never occurs.[1]

We must, therefore, conclude that when an atom of one of these elements has combined with another, it is unable to unite with any more, its affinity being saturated by its union with this single atom. Its capacity of saturation, therefore, only extends to a single other atom.

§ 92. It is obvious that the atoms of those compounds which form compounds belonging to types 2, 3, 4, 5, and 6, must have respectively two, three, four, five, and six times as great a capacity of saturation as those atoms which have just been mentioned. An atom of oxygen really does unite with twice as much hydrogen as an atom of chlorine, and an atom of nitrogen with three times, and an atom of carbon with four times as much hydrogen. In the same way an atom of oxygen or mercury unites with twice as much chlorine as an atom of hydrogen; the latter combines with only one atom of chlorine, whilst the former unites with two. Again, an atom

[1] Non-gaseous compounds containing more than two atoms will be mentioned later.

of boron, phosphorus, or arsenic, combines with three atoms of chlorine, an atom of carbon or silicon, &c., with four, an atom of niobium or molybdenum with five, and an atom of tungsten with six chlorine atoms. But these elements are not able to unite with a larger number. The force of attraction, the affinity, of oxygen, sulphur, selenium, &c., is exhausted by combination with two atoms of the first series, *e.g.* with two atoms of hydrogen. The affinity of nitrogen, phosphorus, and the other members of the third group is exhausted by combination with three atoms, of carbon and silicon with four, of niobium, tantalum, molybdenum by union with five, and of tungsten with six atoms of the first group. The six groups of elements are characteristic of the six selected types, and the six groups are distinguished by the type of their compounds with atoms of the first series.

But some of these elements occur under several types, *e.g.* mercury in I. and II., phosphorus in III. and V., tungsten in V. and VI. But it is clear that the power of saturation of these elements can only be determined from those compounds which contain the largest quantity of the other constituent, since it is not exhausted in the other compounds. Although mercury forms a compound HgCl, it does not belong to the group of elements which combine with one atom of chlorine, since it has the power of combining with a second atom. This subject will be further discussed in section IX.

§ 93. The six groups of elements were formerly distinguished as mono, di, tri, tetra, penta, and hexatomic, or as mono, di, and tribasic, &c.

The first expression is unsuitable, since we cannot very well speak of monatomic atoms.[1]

[1] The expressions 'monatomic,' &c., have long been in use, but they have borne widely different meanings at different times. Berzelius in 1827 (*Jahresber.* Nos. 7, 89) applied the term 'polyatomic' to elements like chlorine or fluorine, several atoms of which unite with a single atom of another element. Gaudin de Saintes made a happy application of the terms 'monatomic, diatomic,' &c., by employing them to express the number of atoms contained in a molecule. He called mercury in the gaseous state a 'gazmonatomique,' since its molecule only contains a single atom. ('Note sur quelques Propriétés des Atomes,' *Bibl. Univ.* Janv. et Févr. 1833; 'Recherches sur la Structure Intime des Corps Inorganiques,' &c. *Ann. Chim. Phys.* 1833, lii. 113. See also Amadeo

The terms 'monobasic,' &c., remind us that the doctrine of polyvalent elements or radicals had its origin in Liebig's classical investigations on polybasic organic acids.[1] But this expression cannot well be applied to the atoms, since, chemically speaking, basic is understood to be opposed to acid. The most correct expression is to speak of the atoms as having 1-, 2-, 3-, 4-, 5-, and 6-fold power of saturation. In many cases it is convenient to speak of the six groups of atoms as having 1, 2, 3, 4, 5, and 6 units of affinity. The terms introduced by Erlenmeyer[2] are shorter and very convenient, viz. mono-, di-, tri-, and tetra-valent. Wislicenus[3] has also proposed the half Greek, half Latin terms monaffine, diaffine, &c. for which the author suggested the substitution of the words, uni-, bi-, tri-, quadri-valent, &c.[4]

Odling's proposal to use the terms monad, diad, triad, &c. has been generally accepted. These expressions were employed by A. W. Hofmann in his 'Introduction to Modern Chemistry,'[5] and proving to be convenient have since come into general use.[6]

For the sake of convenience and conciseness, it is permissible to form the substantives monovalence, divalence, &c., from the adjectives monovalent, divalent, &c.

§ 94. In order to indicate the power of saturation in the formulæ, Odling has proposed to place above the atomic

Avogadro, *Fisica dei Corpi Ponderabili.* Torino, 1837–41' ii. 869.) L. Gmelin (*Handb.* 5. Aufl. i. 50) also termed mono-, di-, and hex-atomic the gases which contained one, two, or six atoms in the same volume. Clausius attaches the same signification to the expression as Gaudin de Saintes. He uses it to indicate the number of atoms which form a molecule. Thus Clausius calls oxygen diatomic because its molecule is composed of two atoms. ('Unterschied zwischen activem und gewöhnlichem Sauerstoff,' *Vierteljahrsschrift der Naturf. Ges. in Zürich*, viii.; *Pogg. Ann.* 1864, cxxi. 261.) This is the only correct use to which these terms, monatomic, &c. can be applied. To use them, as is still frequently the custom, to express the number of hydroxyl groups in a compound, is particularly reprehensible (see section vii.)

[1] *Ann. Chem. Pharm.* 1833, xxvi. 113.

[2] *Zeitschrift f. Chem. u. Pharm.* 1860, 540, and 1862, 25.

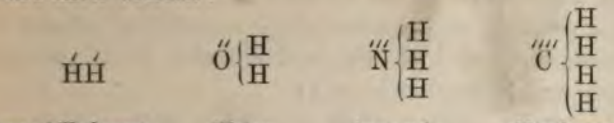
[3] *Ann. Chem. Pharm.* 1863, cxxviii. 2.

[4] First edition of the German *Mod. Theor.* p. 67.

[5] *Introduction to Modern Chemistry*, 1865, 169.

[6] The account given by H. Wichelhaus (*Ann. Chem. Pharm.* 1868, Suppl.-Bd. vi. 257) of the origin of this nomenclature is not quite correct.

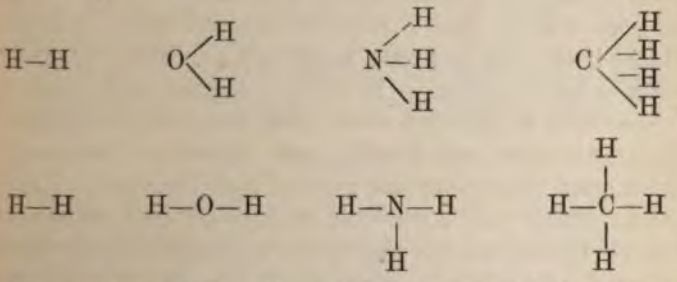
symbols a corresponding number of accents. The four first types are then written :



Type of Hydrogen | Water | Ammonia | Marsh gas

The use of these accents, or of Roman numerals placed above the atomic symbols, has not become general ; it appears, indeed, that they need not be employed now that the views of chemists on the different capacities of saturation of the atoms coincide on all essential points.

Instead of using these accents, A. S. Couper [1] unites the symbol of each element by a line, or series of dots, to the symbol of the atom by the affinity of which it is held in combination ; *e.g.*



The number of lines attached to a symbol of the element indicates the power of saturation of the atom.

§ 95. The connection between the type of a compound and the nature of the atoms contained in it is still more evident when the chemical reactions of the compound are taken into consideration. The type is preserved so long as the typical atom remains in the compound ; it is lost as soon as this atom is expelled.

The anhydride of hypochlorous acid and hydrogen yield water and hydrochloric acid :

$$OCl_2 + HH + HH = OH_2 + HCl + HCl.$$

The oxygen atom retains the type of the compound 1 : 2,

[1] *Chem. Soc. Quart. Journ.* vii. 1.

by reason of its double capacity of saturation; but the chlorine atoms which were united with it form compounds of the type 1 : 1, since they only possess single capacity of saturation.

Phosphoretted hydrogen and chlorine form phosphorous chloride and hydrochloric acid:

$$PH_3 + ClCl + ClCl + ClCl = PCl_3{}^1 + HCl + HCl + HCl$$

Marsh gas and chlorine undergo the following changes:

$$\begin{aligned} CH_4 + ClCl &= CH_3Cl + HCl \\ CH_3Cl + ClCl &= CH_2Cl_2 + HCl \\ CH_2Cl_2 + ClCl &= CHCl_3 + HCl \\ CHCl_3 + ClCl &= CCl_4 + HCl \end{aligned}$$

In these examples the type is preserved by the atom of phosphorus and the atom of carbon. Since every compound is decomposed and loses its type as soon as its characteristic atom is removed without being replaced by another of similar capacity of saturation, it must be assumed that it is this atom which holds the molecule together; *e.g.* every molecule of water is held together by its atom of oxygen, each molecule of ammonia by its nitrogen atom, each molecule of marsh gas by its carbon atom, and, finally, each molecule of molybdenum or tungsten chloride by the atom of molybdenum or tungsten. Atoms which only form with each other compounds of the first or hydrogen type, the atoms of single capacity of saturation do not directly contribute to the preservation of the other types; their single affinity just suffices to link them to the characteristic atom of the type. They appear to exert only an indirect influence, inasmuch as, under certain conditions, each of them can increase or diminish the force by which the polyvalent atom attracts the other monovalent atoms, and can facilitate or hinder its union with the atoms of certain elements.

§ 96. In the preceding cases, only the compounds of polyvalent atoms with monovalent atoms have been considered. If the monovalent atoms are replaced by polyvalent, then very complicated relations may ensue, although the decompositions are frequently of a very simple character.

[1] If chlorine is in excess, PCl_3 is converted into the solid compound PCl_5, which has been mentioned in §§ 30, 31, 32.

When marsh gas is burnt in oxygen, carbon dioxide and water are formed,

$$\overset{\cdots}{C}HHHH + \overset{\cdot\cdot}{O}\overset{\cdot\cdot}{O} + \overset{\cdot\cdot}{O}\overset{\cdot\cdot}{O} = \overset{\cdots}{C}\overset{\cdot\cdot}{O}\overset{\cdot\cdot}{O} + H\overset{\cdot}{H}\overset{\cdot\cdot}{O} + H\overset{\cdot}{H}\overset{\cdot\cdot}{O}$$

Two atoms of oxygen of equal capacity of saturation replace four hydrogen atoms. On the other hand, each atom of oxygen is replaced by two atoms of hydrogen. The four affinities of carbon are now saturated by two divalent atoms, the two affinities of oxygen in carbon dioxide are each saturated by two of the four affinities of carbon, and in water by the two single affinities of two hydrogen atoms. When ammonia burns, nitrogen and water are produced.

$$3O + 2\overset{\cdots}{N}H_3 = \overset{\cdots}{N}\overset{\cdots}{N} + 3\overset{\cdot\cdot}{O}H_2$$

The three affinities of each atom of nitrogen are now satisfied by a single atom of nitrogen instead of by three atoms of hydrogen.

When oxygen is liberated from water by electrolysis, a divalent atom of O replaces two monovalent atoms of H.

$$2H_2\overset{\cdot\cdot}{O} = \overset{\cdot\cdot}{O}\overset{\cdot\cdot}{O} + 2\overset{\cdot}{H}\overset{\cdot}{H}$$

Similar compounds of polyvalent atoms can be referred to the original types by regarding them as derivatives of the original forms of the types, in which the monovalent have been replaced by polyvalent atoms in such a way that the total number of affinities remains unaltered. Thus some of the compounds in the second table (§ 90), *e.g.* CO_2 and CS_2 may be regarded as derivatives of CH_4 in which each atom of sulphur or oxygen has replaced two of hydrogen.

Hence it follows that compounds containing more than one polyvalent atom cannot be arranged in types according to the number of their atoms. For this reason it is not proposed to discuss now the compounds in the second table in § 90.

A polyvalent atom can replace several monovalent atoms belonging to different molecules, which are in this way united to form a single molecule.

In many reactions water is formed from hydrochloric acid by the replacement of chlorine by oxygen. But as chlorine is

monovalent and oxygen divalent, two molecules are united to form one.

$$\begin{matrix}\mathrm{H\,Cl}\\ \mathrm{H\,Cl}\end{matrix} \quad \text{form} \quad \left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}$$

Two molecules of hydrochloric acid. — One molecule of water.

In the same way the hydrogen can be replaced by a polyvalent atom: *e.g.*

$$\begin{matrix}\mathrm{H\,Cl}\\ \mathrm{H\,Cl}\end{matrix} \quad \text{form} \quad \mathrm{Hg}\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\end{matrix}$$

Two molecules of hydrochloric acid. — One molecule of mercuric chloride.

The consideration of these and similar cases has led the water type to be regarded as the 'doubled' type of hydrochloric acid, in which the chlorine has been replaced by the corresponding equivalent quantity of oxygen.

Many compounds, mercuric chloride, for example, are more frequently referred to the doubled first type than to the second, especially when more stress is placed on purely chemical properties than on the number of the atoms and their capacity of saturation.

In a similar way the third, fourth, fifth, and sixth types may be regarded as treble or quadruple the first, &c.

Frequently a partial replacement of the monovalent by the polyvalent atoms takes place, in which case compounds such as the following are produced:

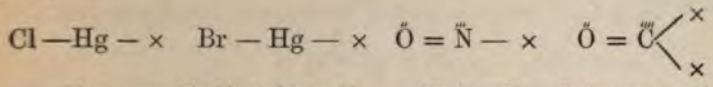
$$\overline{\overline{\mathrm{C}}}\left\{\begin{matrix}\mathrm{Cl}\\ \mathrm{O}\\ \mathrm{Cl}\end{matrix}\right. \qquad \overline{\overline{\mathrm{C}}}\left\{\begin{matrix}\mathrm{N}\\ \mathrm{H}\end{matrix}\right.$$

Phosgene. — Hydrocyanic acid.

The general rule is that the atoms, of whatever description they may be, enter into the molecule in such number that all the affinities are mutually saturated. Hence it follows that since each affinity demands the existence of another by which it is saturated, the sum of all the units of affinity in a molecule must always be an even number.

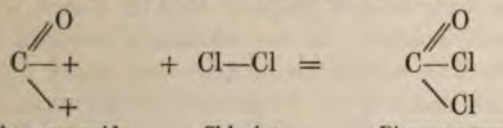
§ 97. Cases are also known, which are of great theoretical interest, in which the affinities of an atom are not completely

saturated. Some of the compounds contained in both the tables in § 90 belong to this class of incompletely saturated compounds.



Mercurous chloride and bromide. Nitric oxide. Carbon monoxide.

The unusual facility with which these bodies enter into combination is the result of their exceptional constitution. The spontaneous oxidation of nitric oxide is well known as the essential condition of the sulphuric acid manufacture; the power of carbon monoxide to combine directly with chlorine when exposed to the sun's rays is also well known.



Carbon monoxide. Chlorine. Phosgene gas.

All combinations of atoms with imperfectly saturated affinities behave like carbon monoxide and nitric oxide. Such an atomic group frequently acts like a single atom, resembling a mono-, di-, tri-, or tetra-valent atom, according as it requires one, two, three, four or more monovalent atoms to completely saturate its affinities.

The behaviour of such groups of atoms led Lavoisier to assume the existence of compound radicals; an assumption which, though severely criticised, has, perhaps even for this very reason, largely contributed to the growth of the science of chemistry.

In a somewhat different sense these radicals have more recently been termed 'rests' (*residus*) by Gerhardt, and 'incomplete molecules' by Wislicenus.

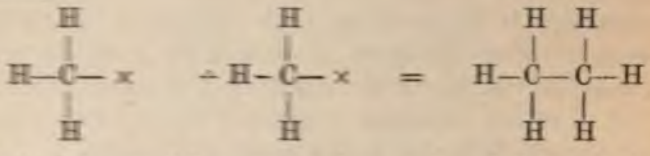
In the present state of our science, it can no longer be doubted that the imperfectly saturated molecules do really behave analogously to isolated simple atoms. The similarity arises from the fact that in each case the affinities are not completely saturated, and that both the radical and the atom contain one or more unsaturated units of affinity. Each atom or radical possesses the unusual activity which is characteristic

of the *status nascendi*, until it unites with another non-saturated atom or radical.

When two atoms of hydrogen come in contact with each other, they form the compound known as 'free hydrogen:'

$$H + H = H\widehat{H}$$

If two methyl radicals meet they form 'free methyl' or 'dimethyl.'



It is owing to this property that so few of these radicals have been isolated. It was obviously incorrect to deny the existence of these radicals because they could not be isolated. Only those radicals can be isolated the affinities of which are under certain conditions comparatively weak. Formerly there was a tendency to regard as radicals those groups of atoms only which could be isolated, but at the present time the impossibility of their existence in the free state would be more probably considered as their characteristic feature.[1]

§ 98. It is not by any means necessary that the radicals which unite together should be of the same description. The radical methyl CH_3 as well as the hydrogen atom H can unite with the radical hydroxyl OH:

$$H + \left.\begin{matrix}\times\\ H\end{matrix}\right\rangle O = \left.\begin{matrix}H\\ H\end{matrix}\right\rangle O \quad \text{Water}$$

$$(CH_3) + \left.\begin{matrix}\times\\ H\end{matrix}\right\rangle O = \left.\begin{matrix}(CH_3)\\ H\end{matrix}\right\rangle O \quad \text{Methyl alcohol}$$

[1] Liebig's classic definition of a compound radical still holds good. In his treatise (1838) 'Ueber Laurent's Theorien der organischen Verbindungen,' *Ann. Pharm.* xxv. 1, he says: 'We call cyanogen a radical because (1) it is the invariable constituent in a series of compounds; (2) because it can be replaced in these compounds by other simple bodies; (3) because in its compounds with a simple body the latter can be replaced by equivalents of other simple bodies.'

Two at least of these three chief characteristics of a compound radical must be fulfilled before a group of elements can be regarded as a radical.

In most cases 'the organic radicals only exist in our imagination, but their real existence is as little to be doubted as is that of nitric acid [*i.e.* the anhydride N_2O_5, which was not known at that time], although this body is as much unknown as ethyl.'

If the compound radical methyl is regarded as analogous to the single atom of hydrogen, methyl alcohol may be considered as belonging to the type of water. It is derived from water by replacing half the hydrogen by methyl. This method of simplification is often employed. It is only by its use that a systematic survey of the numerous compounds of carbon can be gained. By such methods of simplification the existence of the fourth type was completely overlooked at first and afterwards its use avoided by regarding its chief representative, marsh gas, as methyl hydride, and classing it in the first or hydrogen type.

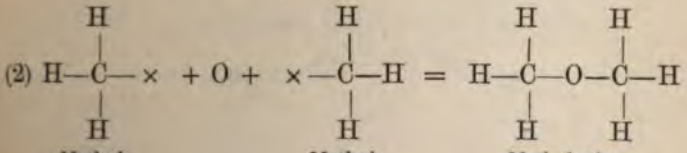
$$C\left\{\begin{matrix}H\\H\\H\\H\end{matrix}\right. = (CH_3)H$$

In this case this method of simplifying the type has been a consequence rather of its origin than a dictate of convenience, and has, therefore, become obsolete ; in other cases it is of essential service, *e.g.* the chemical properties of methyl chloride are clearly and concisely expressed by the formula $(CH_3)Cl$.

It is obvious, however, that a great deal is left to individual caprice. For example, when two methyl radicals (each of which possesses a free affinity) are united to a closed molecule by an atom of oxygen, the resulting compound (methyl ether) may be just as well classed in the water type (1) as in the double marsh gas type (2).

(1) $(CH_3) + O + (CH_3) = \left.\begin{matrix}(CH_3)\\(CH_3)\end{matrix}\right\}O$

Methyl. Methyl. Methyl ether.

(2)


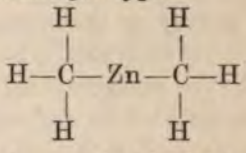
Methyl. Methyl. Methyl ether.

In each molecule an atom of hydrogen is replaced by the equivalent quantity of oxygen, and the two molecules are united to form a single one by the indivisibility of the divalent atom of oxygen.

In the same way zinc methide may be regarded as belonging to the second type

$$\left.\begin{matrix}(CH_3)\\(CH_3)\end{matrix}\right\}Zn$$

or to the doubled marsh gas type



or finally by comparing methyl hydride with hydrogen gas, it may be considered as belonging to the doubled first type.

$\frac{H\ H}{H\ H}$	$\frac{(CH_3)\ H}{(CH_3)\ H}$	$\left.\begin{matrix}(CH_3)\\(CH_3)\end{matrix}\right\}Zn$
Two molecules of hydrogen.	Two molecules of methyl hydride.	One molecule of zinc methide.

The latter method of representing zinc methide is the one which is most frequently used by chemists, but methyl ether is generally compared to the second or water type.

§ 99. The substitution of radicals for atoms enabled Gerhardt[1] to class all the well-known organic compounds under the three first types. In this way he obtained a uniform and systematic classification of organic compounds, such as had never before been attained.

In the chief and secondary types Gerhardt substituted other atoms or organic radicals for one or more hydrogen atoms, and in this way obtained formulæ for numerous inorganic and organic compounds which very clearly showed the analogies in the behaviour of different substances to be a result of their similar composition.

In addition to the following simple types

Chief	Secondary Types.				
$\left.\begin{matrix}H\\H\end{matrix}\right\}$	$\left.\begin{matrix}H\\Cl\end{matrix}\right\}$	$\left.\begin{matrix}H\\Br\end{matrix}\right\}$	$\left.\begin{matrix}H\\I\end{matrix}\right\}$	$\left.\begin{matrix}H\\F\end{matrix}\right\}$	$\left.\begin{matrix}H\\Cy\end{matrix}\right\}$
$\left.\begin{matrix}H\\H\end{matrix}\right\}O$	$\left.\begin{matrix}H\\H\end{matrix}\right\}S$	$\left.\begin{matrix}H\\H\end{matrix}\right\}Se$	$\left.\begin{matrix}H\\H\end{matrix}\right\}Te$		
$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$	$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}P$	$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}As$	$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}Sb$		

[1] *Traité de Chimie Organique.* Paris, 1853–6. See specially vol. iv. pp. 561-866

Gerhardt also doubled and trebled these types for compounds which are formed, or which may be considered to be derived, from them by the substitution of polyvalent atoms or radicals for the hydrogen atoms of the different molecules.

Double Types.

$$\left.\begin{matrix}H_2\\H_2\end{matrix}\right\} = \left.\begin{matrix}H\\H\\H\\H\end{matrix}\right\} \qquad \left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2 = \left.\begin{matrix}H\\H\end{matrix}\right\}O \left.\begin{matrix}\\\\H\\H\end{matrix}\right\}O \qquad \left.\begin{matrix}H_2\\H_2\\H_2\end{matrix}\right\}N_2 = \left.\begin{matrix}H\\H\\H\end{matrix}\right\}N \left.\begin{matrix}\\\\H\\H\\H\end{matrix}\right\}N \qquad \&c.$$

Types.

H_2Cl_2	CO, Cl_2 Phosgene.	SO_2, Cl_2 Sulphuryl chloride.	
H_3Cl_3	B, Cl_3 Boron chloride.	P, Cl_3 Phosphorous chloride.	PO, Cl_3 Phosphorus oxychloride.
$\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2$	$\left.\begin{matrix}SO_2\\H_2\end{matrix}\right\}O_2$ Sulphuric acid.	$\left.\begin{matrix}C_2O_2\\H_2\end{matrix}\right\}O_2$ Oxalic acid.	$\left.\begin{matrix}C_4H_4O_4\\H_2\end{matrix}\right\}O_2$ Tartaric acid.
$\left.\begin{matrix}H_3\\H_3\end{matrix}\right\}O_3$	$\left.\begin{matrix}B\\H_3\end{matrix}\right\}O_3$ Boric acid.	$\left.\begin{matrix}B\\B\end{matrix}\right\}O_3$ Boric anhydride.	$\left.\begin{matrix}C_6H_5O_4\\H_3\end{matrix}\right\}O_3$ Citric acid.
$\left.\begin{matrix}H_2\\H_2\\H_2\end{matrix}\right\}N_2$	$\left.\begin{matrix}(CH_3)_2\\C_2O_2\\H_2\end{matrix}\right\}N_2$ Dimethyl oxamide.	$\left.\begin{matrix}(C_7H_5)_3\\\\H_3\end{matrix}\right\}N_2$ Hydrobenzamide.	$\left.\begin{matrix}H_2\\CO\\H_2\end{matrix}\right\}N_2$ Urea.
$\left.\begin{matrix}H_3\\H_3\\H_3\end{matrix}\right\}N_3$	$\left.\begin{matrix}C_6H_5O_4\\H_3\\H_3\end{matrix}\right\}N_3$ Citramide.	$\left.\begin{matrix}C_6H_5O_4\\(C_6H_5)_3\\H_3\end{matrix}\right\}N_3$ Citranilide.	$\left.\begin{matrix}(CO)_3\\\\H_3\end{matrix}\right\}N_3$ Cyanuric acid.

Gerhardt did not make any definite distinction between the typical atoms and those replacing them, but on the contrary he sometimes regarded the former and sometimes the latter as typical, according to the decomposition represented and the analogies of character which he wished to indicate.

For example, he wrote,

Cyanic acid $\left.\begin{matrix}CN\\H\end{matrix}\right\}O$, or $\left.\begin{matrix}CO\\H\end{matrix}\right\}N$

Benzaldehyde $H.C_7H_5O$, or $\left.\begin{matrix}C_7H_5\\H\end{matrix}\right\}O$, and so on.

But many chemists regarded such a mutability of the formulæ with suspicion, and considered that only certain atoms were typical of each substance, hence there was considerable discussion, much of which we now regard as idle, on the value of different formulæ.[1] Each author adhered more firmly to his own formulæ as these increased in number.

Since the radicals used in referring all compounds to a few types were frequently very complex, Gerhardt endeavoured to simplify them. He applied the term 'copula' to those groups of atoms in the radical which appeared to exert a comparatively slight influence on the characteristic properties of the bodies, and termed the radicals composed of such groups 'conjugated,' *i.e.* simple radicals in which one or more atoms have been replaced by complicated radicals; *e.g.*—

$\left.\begin{matrix} C_2H_3O \\ H \end{matrix}\right\}O$ Acetic acid.

$\left.\begin{matrix} C_2(Cl_2)HO \\ H \end{matrix}\right\}O$ Dichloracetic acid.

$\left.\begin{matrix} C_2(Cl_3)O \\ H \end{matrix}\right\}O$ Trichloracetic acid.

or

$\left.\begin{matrix} CO(CH_3) \\ H \end{matrix}\right\}O$

Acetic acid, analogous to methyl sulphurous acid.[2]

$\left.\begin{matrix} SO_2 \cdot (CH_3) \\ H \end{matrix}\right\}O$

$\left.\begin{matrix} C_7H_5O \\ H \end{matrix}\right\}O$ Benzoic acid.

$\left.\begin{matrix} C_7H_4(NO_2)O \\ H \end{matrix}\right\}O$ Nitrobenzoic acid.

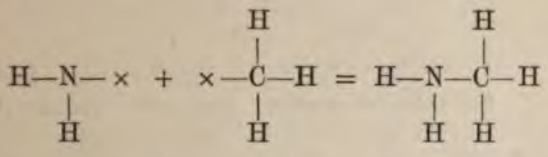
$\left.\begin{matrix} C_7H_3(NO_2)_2O \\ H \end{matrix}\right\}O$ Dinitrobenzoic acid.

This idea of couples as used by Gerhardt was in itself quite harmless, as the formulæ he used for a substance varied according to the analogies of character he wished to emphasise, but it acquired from Berzelius and others an exaggerated importance, productive of much confusion and debate.[3]

The composition of the radicals by repeated substitution became more complicated, the formulæ became the more remarkable, as it was generally assumed that the substituted radicals were contained within the radical the hydrogen atoms of which they had replaced. Although this idea could

[1] See Laurent, *Méthode de Chimie*, p. 27; Kekulé, *Lehrb.* i. 58.
[2] *Traité de Chimie Organique*, iv. 672.
[3] Laurent, *loc. cit.* p. 249.

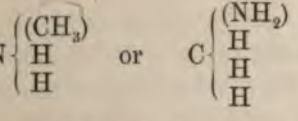
not always be graphically represented, a distinction was made between the radical which was substituted and the radical in which the substitution took place, although it is obviously a matter of choice whether methylamine, for example,



which is formed from ammonia and methyl iodide, according to the equation

$$ICH_3 + NH_3 = IH + NH_2CH_3,$$

be regarded as



i.e. whether it is ammonia in which an atom of hydrogen has been replaced by methyl (CH_3), or marsh gas in which an atom of hydrogen has been replaced by the amide group (NH_2). In reality, each radical replaces an atom of hydrogen in the other; both formulæ are therefore equally correct. The former is generally preferred, as methylamine in its properties more closely resembles ammonia than marsh gas. In complicated compounds—the aromatic, for example—formulæ of the second pattern are frequently used.

An important extension in the manner of using types was introduced by Kekulé.[1] He regarded what had previously been considered as conjugated compounds as combinations of different types, as mixed types formed by the replacement of a portion of the monovalent atoms in two or more molecules of different types, by a polyvalent atom or radical, thus bringing about the union of several molecules.

[1] 'Ueber die sogenannten gepaarten Verbindungen und die Theorie der mehratomigen Radicale,' *Ann. Chem. Pharm.* 1857, civ. 129–150.

The following compounds may be regarded as belonging to mixed types:

Types			
$\left.\begin{matrix}H\\H\end{matrix}\right\}$	$K\left\{\begin{matrix}SO_2\\H\end{matrix}\right\}O$	$CH_3\left\{\begin{matrix}CO\\H\end{matrix}\right\}O$	$Cl\left\{\begin{matrix}SO_2\\H\end{matrix}\right\}O$
	Acid potassium sulphite.	Acetic acid.	Chlorosulphonic acid.
$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N\left\{\begin{matrix}\\\\H\end{matrix}\right\}O$	$H\left\{\begin{matrix}CO\\H\end{matrix}\right\}N\left\{\begin{matrix}\\\\H\end{matrix}\right\}O$	$H\left\{\begin{matrix}C_2O_2\\H\end{matrix}\right\}N\left\{\begin{matrix}\\\\H\end{matrix}\right\}O$	$H\left\{\begin{matrix}C_2H_2O\\H\end{matrix}\right\}N\left\{\begin{matrix}\\\\H\end{matrix}\right\}O$
	Carbamic acid.	Oxamic acid.	Glycocoll.

This extension of the system of types soon led to the disuse of Gerhardt's limited types. Gerhardt's types have rendered great service in the development of the science, but they can only be regarded as a part of the scaffolding which was removed when the erection of the system of organic chemistry had made sufficient progress to be able to dispense with it. The comparison of a large number of compounds with a small number of types afforded numberless opportunities of reviewing individual cases in a variety of ways; cases of analogy and of contrast thus became apparent, and finally a general survey of the remarkable behaviour of the chemical atoms in their compounds was acquired.

VII.

THE LAW OF ATOMIC LINKING.

§ 100. The laws which express our present knowledge of the actions of affinity are the results of speculations similar to the preceding.

These laws, which now surprise us by their remarkable simplicity, were discovered by attention being directed to the atoms themselves rather than the compound radicals. With the rapid development of chemistry the necessity for extending our speculations to the atoms was more and more felt. This necessity appears to have been recognised almost simultaneously by different chemists. Kekulé was the first to give definite expression to such an opinion, and to fully appreciate its importance; he set forth the argument in a paper published in 1857, entitled *Ueber die sogenannten gepaarten Verbindungen und die Theorie der mehratomigen Radicale*, in which he also explains some of his views on the constitution of chemical compounds. A. S. Couper [1] still more emphatically demanded that the atoms should be studied, and at the same time he thoroughly investigated some of their properties, especially those of the carbon atom, which Kekulé had merely alluded to. Kekulé's views were afterwards more thoroughly developed in several articles, and more especially in his treatise.

The revival of the study of the atoms themselves led to the achievement of what had constituted the aim of all previous effort in theoretical chemistry, viz. the knowledge of the manner in which chemical affinity of the atoms determines the internal constitution of compounds. The individual atoms by the juxtaposition of which a chemical compound is formed are not, as was formerly assumed, retained in the compound, by each atom being subject to the attraction of all or a great

[1] See note to § 94; also *Ann. Chem. Pharm.* 1859, cx. 46, 51.

number of the other atoms, and held in its place by these numerous attractions. This attraction only acts from atom to atom; each atom being attached only to its immediate neighbours as the links of a chain are strung together. No link of the chain can be removed without breaking the continuity.

But all atoms have not the same value as links of a chain. The monovalent atoms resemble those links which are only provided with a single ring or hook, and can therefore only be attached to a single other link. If the second atom is also monovalent, it is impossible to attach a third member. But if the second atom is polyvalent, only one of its units of affinity is required to attach it to the first atom; the remainder can serve to prolong the chain by attaching new members. The possibility of extending the chain ceases as soon as a monovalent atom is added as a terminal link. In this way it is easily seen that an exceedingly large number of chemical compounds are possible, and in fact the existence of innumerable compounds, especially those of carbon, the so-called organic compounds, depends on this peculiar behaviour of the atoms.

It also follows that the number of compounds must be larger in the case of tetravalent than trivalent atoms, and larger for trivalent than divalent atoms.

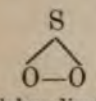
§ 101. In every divalent atom both its affinities are used to attach it to its two neighbours. If a chain is composed solely of divalent atoms, only one affinity can remain free at each end of the chain. When each of these affinities is saturated by a monovalent atom the chain is closed. Sulphuryl chloride and the corresponding bromine compound[1] form such simple chains:

Cl-O-S-O-Cl. Br-O-S-O-Br.

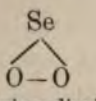
Each of these compounds contains two monovalent atoms, the maximum which can be obtained in a compound composed of mono- and di-valent atoms.

[1] Sulphur and selenium are here regarded as divalent, according to the formerly accepted views. In section IX. a different view, which is probably more correct, will be discussed, according to which these elements are not divalent in these compounds. The above formulæ must therefore be merely regarded as general illustrations.

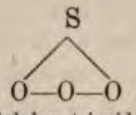
But it may also happen that the affinities of the two end links are satisfied by one divalent instead of two monovalent atoms, *e.g.*



Sulphur dioxide.



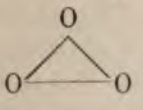
Selenium dioxide.



Sulphur trioxide.

If the molecule of sulphur at a temperature slightly above its boiling point consists of six atoms, as is indicated by its vapour density 6·6, these atoms, in order that all their affinities may be saturated, must also be considered to be arranged in a ring.[1]

If the assumption of Clausius,[2] Soret,[3] and others that



the molecule of ozone contains three atoms be accepted, then ozone must also be represented by a ring-shaped formula.

The number of atoms which unite to form a molecule is never very large in compounds composed only of divalent or of di- and mono-valent atoms. Seven is the largest number of divalent atoms which has up to the present been observed to occur in a molecule of a gaseous compound. This number exists in pyrosulphuryl chloride, $S_2O_5Cl_2$.

§ 102. When a molecule contains tri- and tetra-valent[4] atoms, the number of atoms in a molecule may be very large. The number of monovalent atoms which may be contained in the molecule increases with the number of tri- and tetra-

[1] It is scarcely necessary to remark that the expression 'ring-shaped' need not be accepted as applying to space; it only indicates that the attractions between the atoms which maintain the coherence of the molecule form a continuous series.

[2] 'Ueber den Unterschied zwischen activem und gewöhnlichem Sauerstoffe,' *Vierteljahrsschrift d. Naturf. Ges. in Zürich*, 1863, viii. 345; also *Pogg. Ann.* 1864, cxxi. 250.

[3] 'Recherches sur la densité de l'ozone,' *Compt. Rend.* 1865, lxi. 941 1867, lxiv. 904.

[4] Penta- and hexa-valent atoms are left out of consideration, as at present only a few gaseous compounds containing them are known.

valent atoms. Each tri- or tetra-valent atom uses only one of its units of affinity in uniting with one of the atoms already contained in the molecule, and saturates only one of the affinities of that atom. The addition of each new atom always neutralises at least two units of affinity. But since each trivalent atom adds three and each tetravalent atom four new affinities, it is clear that the number of affinities which are not required for the coherence of the molecule regularly increase with the addition of tri- and tetra-valent atoms. But these affinities may be saturated by monovalent atoms without endangering the stability of the molecule.

§ 103. There is a simple relation between the number of monovalent atoms which can possibly exist in the molecule of any given compound and the number of tri- and tetra-valent atoms in that molecule. This relation may be represented by a general formula. It is obvious that if n represents the number of polyvalent atoms in a molecule, $2(n-1)$ affinities will be required to unite them together, *i.e.* two less than double the number of atoms; for at least two affinities are satisfied by the union of the first two atoms, and two more for the addition of every new atom.

Let n_2 be the number of divalent atoms, n_3 the tri-, n_4 tetra-, n_5 penta-, and n_6 the number of hexa-valent atoms in a molecule of the compound, then:

$$n_2 + n_3 + n_4 + n_5 + n_6 = n;$$

and let s be the sum of their units of affinity or capacity of saturation, then:

$$2n_2 + 3n_3 + 4n_4 + 5n_5 + 6n_6 = s;$$

the number of monovalent atoms n_1 which can possibly be contained in the compound is then determined by the equation

$$n_1 \leqq s - 2(n-1),$$

or by replacing the values for s and for n:

$$n_1 \leqq n_3 + 2n_4 + 3n_5 + 4n_6 + 2.$$

The number n_1 of monovalent atoms is therefore independent of the number of divalent atoms n_2. Every compound,

of whatever nature it may be, may always contain at least two monovalent atoms, and one more for each additional trivalent, and two for each additional tetravalent atom.

§ 104. In a compound of carbon, nitrogen, oxygen, and hydrogen of the composition $C_xN_yO_zH_w$ when

$$n_1 = w,\ n_2 = z,\ n_3 = y,\ n_4 = x,\ n_5 = o \neq n_6,$$

the number of hydrogen atoms is shown by the equation

$$w \leqq 2x + y + 2.$$

The largest quantity of hydrogen which could be contained in such a compound would be

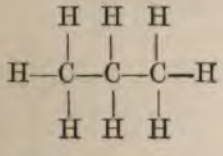
$$w = 2x + y + 2.$$

Not one of the thousands of the compounds of carbon (in the gaseous state) contains more than this amount of hydrogen.

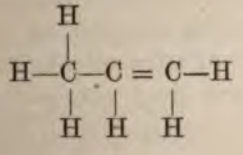
But the number of hydrogen atoms may be less than this formula indicates. This occurs when the polyvalent atoms are mutually united by more than $2(n - 1)$ affinities.

For instance, a hydrocarbon with three carbon atoms in the molecule cannot contain more than $3 \times 4 - (2 \times 3 - 2) = 2 \times 3 + 2 = 8$ atoms of hydrogen.

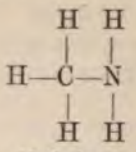
The group of atoms



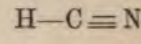
cannot take up more than the eight monovalent atoms without decomposing. But if two carbon atoms each mutually saturate more than one of their affinities, then the number of hydrogen atoms will be diminished by two:



In the same way, the union of an atom of carbon and an atom of nitrogen with hydrogen forms the combinations



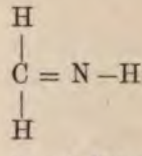
Methylamine.



Hydrocyanic acid.

In the first case the carbon atom only saturates one affinity, and in the second case all the three affinities of the nitrogen. In the first case five affinities remain for hydrogen, in the second case only one.

An intermediate compound is also possible, although it is not known at present:



in which three affinities are saturated by hydrogen.

§ 105. The mutual neutralisation of the polyvalent atoms always diminishes the number of the monovalent atoms by an even number, 2, 4, 6, &c. The number of atoms, therefore, remains even or uneven, according as it is even or uneven in the compound richest in hydrogen.

But the equations

$$n_1 = n_3 + 2n_4 + 2 = n_3 + 2(n_4 + 1)$$

or

$$n_1 - n_3 = 2(n_4 + 1)$$

show that the difference $n_1 - n_3$, and consequently the sum $n_1 + n_3$ must always be an even number: n_1 is even when n_3 is even, and *vice versâ*.

Laurent[1] termed the tri- and mon-atomic elements, between which no distinction was made in his time, 'diads,' because the atoms of this class enter into combination in pairs (because $n_1 + n_3$ is always an even number), as distinguished from the 'monads,' *i.e.* the di- and tetra-valent elements which can enter into a compound in any given number.

[1] *Méth. de Chimie*, p. 58.

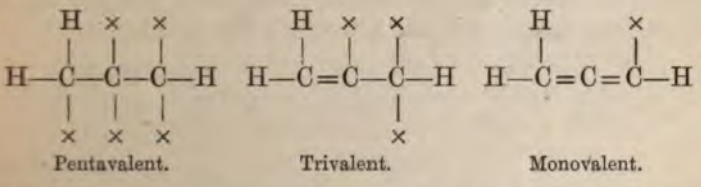
§ 106. It follows from the preceding that in a group of atoms, which plays the part of a compound radical, some of the affinities of the polyvalent atoms must remain unsaturated, and the following equation must hold good :

$$n_1 \angle n_3 + 2n_4 + 3n_5 + 4n_6 + 2.$$

The difference, $(n_3 + 2n_4 + 3n_5 + 4n_6 + 2) - n_1$, shows the maximum number of monovalent atoms which the radical can replace. But the number may be diminished (always by an even number) by the affinities of two or more polyvalent atoms mutually saturating each other.

The radical C_3H_3 is pentavalent; since $n_4 = 3$, $n_6 = n_5 = n_3 = o$, and $n_1 = 3$; then $2 . n_4 + 2 - n_1 = 2 . 3 + 2 - 3 = 5$.

By the mutual combination of the C atoms the radical may become tri- or mono-valent :



Similarly the radical C_3H_4 may be tetra- or di-valent, or saturated according as the three carbon atoms use four, six, or eight of their twelve units of affinity for union with each other.

§ 107. The structure of a molecule may become very complicated by this multiple union of polyvalent atoms. It is only in the simplest cases that the chain of atoms is linear ; but if a polyvalent atom is attached to a tri- or tetra-valent member of the chain, a new series may be linked on to this atom. If a tri- or tetra-valent atom which is already combined to two others (and consequently occupies a position inside the chain) unites with a third polyvalent atom, then other atoms can attach themselves to this new member. In this way a branched series of atoms is obtained composed of several linear chains. In the same way these branches can also divide, and the new branches may be united together by connecting links, forming ring-shaped or netlike structures.

In this way very complicated relations arise which are difficult of solution.[1]

The stable radicals of the so-called aromatic series (benzene, naphthalene, anthracene) have in all probability a constitution similar to one another, containing a series of carbon atoms united to form a ring.

The organic compounds of the highest order, the substances which are the essential supporters of the life of plants and animals, have in all probability a structure resembling a chain composed of many links, and divided into several branches. The arrangement of the atoms in the simpler compounds is generally linear, or resembles a chain having a small number of branches.

Branched chains of atoms not infrequently occur, even amongst the more simply constituted compounds. The three ethyl radicals in tri-ethylamine form three straight chains, which meet together in the nitrogen atom as a centre :

$$N\begin{cases}C_2H_5\\C_2H_5\\C_2H_5\end{cases} \qquad \text{or} \qquad N\begin{cases}CH_2—CH_3\\CH_2—CH_3\\CH_2—CH_3\end{cases}$$

§ 108. If we ask for an explanation of the remarkable fact that certain atoms only unite with one other atom, some with two, and others again with three, four, five, or six atoms, and that when they have united with these they can no longer combine with any more, we find that chemistry is in the same position that it has been for the last century. The question is only a more definite form of the question why one molecular weight of nitric acid only saturates one equivalent of potash, instead of two equivalents, like sulphuric acid, or three, like phosphoric acid. We do not even clearly understand what is fully implied by the expression ' saturates.'

This limited action of affinity is either due to the fact that the combined atoms occupy the space in which the affinity can assert itself, *i.e.* occupy the sphere of action so that no more new atoms can approach, or else it is due to the fact

[1] The possibility of the existence of this class of compounds was first pointed out by Couper, *loc. cit.*

that the atoms lose their power of entering into combination after they have once combined.

The first explanation requires the assumption that each monovalent atom possesses only a single position in space in which another atom can be held by it in a state of stable equilibrium. A divalent atom would have two, a trivalent three, tetra-, penta-, hexa-valent atoms would have four, five, or six such positions. But the six kinds of atoms must be of such a nature that a monovalent atom occupies only one of these positions, while di- and tri-valent atoms extend over two or three respectively.[1]

According to this idea, the force by which two atoms are mutually attracted finds its mathematical expression in a function which depends not only on the distance between the atoms, but also on the co-ordinates of certain axes within the atoms, and would attain a maximum for certain values of these co-ordinates.[2]

The second explanation, viz. that combination changes the atoms in such a way that their force of attraction is exhausted, like that of a laden magnet, resembles the basis of the electro-chemical theory of Berzelius.

But it appears difficult to replace the untenable assumptions of this theory by more suitable hypotheses. It is not improbable that these phenomena are related to electrical phenomena, but the knowledge of the connection between electrical and chemical phenomena has scarcely advanced

[1] The atoms are not in a state of rest at these centres of attraction; on the contrary, they are in a state of active motion, with these points as centres of equilibrium. The motion may be rotary or oscillating. In those cases in which an atom fills two or more of these points, it is considered to oscillate between or, rotating, pass through these centres.

[2] A function satisfying these conditions is obtained by the assumption of definitely arranged positive and negative electric masses within the atom, the attraction or repulsion of which rapidly diminishes with the distance. We may imagine the division into positive and negative masses, arranged in such a way that both atoms are in a state of rest only in certain relative positions, so that when they are brought closer together repulsion ensues, and when they are removed farther apart attraction ensues. Finally, a lateral displacement would restore them to a state of equilibrium. But as we are completely in the dark concerning the nature of electricity, hypotheses of this description are unprofitable.

beyond the views [1] held by Davy that the two phenomena are distinct, although produced by the same power, acting in the one case on finite masses and in the other on the smallest particles of these masses.

§ 109. After the empirical discovery of the general law of the combination of atoms to form compounds, viz. the law of atomic linking, the next problem of the science is to discover the arrangement and position of the atoms in every compound, or, to use the customary expression, to investigate the rational formulæ of compounds.

The investigation of the manner in which the atoms are arranged is older than the knowledge of the law of atomic linking. The latter is only a result of this laborious research, which had often been declared to be vain and fruitless. The investigation has acquired from this law a more clearly defined goal, to which, by the unwearying labour of numerous investigators, it is rapidly advancing.

The clearer conception of the problem gained by the knowledge of atomic linking gave rise to the proposal of a new mode of expressing the new form of the problem. In the course of time several methods of expressing the manner in which the atoms are united together in a compound have come into use. Berzelius, the originator of our present system of chemical symbols, distinguished between the empirical and rational formulæ of chemical compounds. The former merely express the composition from the quantitative determination of the constituents, but the latter also show the manner in which the constituents are supposed to be combined. The inexact expression, 'the rational composition of a compound,' is occasionally used, by which is meant the rational expression of the composition.

According as more or less importance has been attached to graphic representation, the following expressions have been used: 'position or arrangement of the atoms,' or the

[1] In a paper read before the Royal Society, Nov. 2, 1806. See also Berzelius's *Jahresber.* 1826, vii. 19; Davy's *Elements of Chemical Philosophy*, 1812, p. 165; *Collected Works*, 1840, iv. 120. 'They are conceived, on the contrary, to be distinct phenomena, but produced by the same power, acting in one case on masses, in the other on particles.'

more general expression, 'chemical constitution' of the compound. Since the discovery of the chain-like union of the atoms Butlerow[1] has proposed to substitute for these expressions the term 'chemical structure.'

This innovation is, however, unnecessary, since the word 'constitution' conveys exactly the same meaning as Butlerow's term 'structure.' If it is desired to lay especial stress on the fact that the notions now in vogue regarding the nature of the combination of the atoms differ from those formerly held, then it is obvious that expressions should be employed which clearly indicate this distinction. But this essential difference lies, as was pointed out in the first edition of the German version of this book in 1864, in the assumption of the chain-like linking of the atoms; this assumption is most clearly and concisely expressed by terming the constitution or structure, 'atomic linking.' There is no reason why one expression should be used in preference to, or to the exclusion of, the others; there is still less reason for the energetic discussions which have taken place on this subject. In the following pages these terms will be used as more or less synonymous.

§ 110. Whatever form of expression is used, it is undeniable that extraordinary progress has been made. At the present time all efforts are directed to the investigation of relations which were formerly regarded by many chemists, but not by all, as subjects which could never be properly investigated. At the present time we consider this research difficult, but we have numerous proofs in the results which we have already gained that it is not only capable of solution, but that it also affords a very fruitful field for the spirit of investigation.

But we are only at the commencement of the solution of this problem; our auxiliaries have not yet been sufficiently developed. It is very probable that the law of atomic linking, as it is known at the present day, is merely a special case of the general law which governs the combination of atoms. At first it was only valid for gaseous compounds, and was

[1] *Zeitschr. f. Chem. Phar.* 1861, 553; Butlerow, *Lehrbuch der org. Chem.* Leipzig, 1868, 36.

deduced from the molecular weights of such substances; it is indicative, however, of the structure of many compounds which are not capable of existing in the gaseous state.

It is especially applicable, without reference to the state of aggregation, to the innumerable multitude of carbon compounds. The investigation of the constitution of these bodies is a problem of great extent and of great difficulty. In the present stage of its development organic chemistry, *i.e.* the chemistry of the carbon compounds, no longer directs its efforts solely to the discovery of new compounds, but also to the unravelling of the inner nature of known compounds. At the beginning of the present century this science could scarcely give with certainty the composition of a few organic compounds. Since then it has not only investigated the enormous amount of material offered by nature, but has continually created new material, over which it has extended its dominion.

But the extension of territory has always been accompanied, though not always at the same rate, by the investigation and arrangement of the newly acquired province. This has now become the chief problem of the science.

Investigation is now specially directed to acquiring a knowledge of the arrangement of the atoms in the molecule. The causes which compel the atoms to assume, change, or deviate from this order are only secondary subjects in the investigation.

Chemistry is working at a doctrine of equilibrium, a statics of the atoms, with which the doctrine of the motion of the atoms, the dynamics, is closely related.

§ 111. The discovery of the manner in which the atoms are united together in a molecule of a given compound presupposes the knowledge of

1. The molecular weight;

2. The nature and number of the atoms entering into the composition of the molecule; and

3. The chemical value of the power of saturation of these atoms.

The molecular weight is determined by Avogadro's law; the number and nature of the atoms contained in the molecule

is found by the chemical analysis or synthesis of the compound. The chemical value of each element is determined from the composition of its most simple compounds. Formerly the valence was generally deduced from the compounds tabulated in § 90.

Important and valid reasons have been advanced against the general use of the equivalence of the atoms as determined in this way, which will be more fully discussed in section IX. In the present instance it is assumed that the valence of all the elements in question is known.

When only the composition and not the molecular weight is known, the latter is often assumed hypothetically by regarding the formula deduced from analysis as the molecular weight. Of course all further conclusions stand or fall with the correctness of this assumption, on which they are based. We start with the assumption that both the composition and the molecular weight are known.

As a rule, the structure is discovered more easily when the molecule only contains a small number of atoms and a small number of elements. The difficulty, as a rule, increases with the addition of polyvalent atoms, since they can produce double linkings. On the other hand, a relative increase in the number of monovalent atoms usually makes the problem easier by limiting or preventing the possibility of the atoms combining to form closed chains, and the possibility of unsaturated affinities.

When the molecular weight of a compound is given, and the number and nature of the atoms forming the molecule are known, the first problem to be solved is to determine all the possible forms of combination which these atoms can form, according to their nature and number. This first problem is purely mathematical, and can be solved by the methods of combinations, permutations, and variations. If the answer to this question indicates several forms of combination, then it appears that it is possible for several compounds to exist which contain the same constituents arranged differently. Conformably with this result of theory, experience has long since shown that compounds frequently occur which are identical in composition, but possess different properties.

Such bodies are said to be isomeric or isomerides. If these isomeric compounds have the same molecular weight, then the difference in their properties can only be due to a difference in the atomic linking. Such isomeric compounds are said to be metameric. But if the molecular weight of one compound is a multiple of the other, then they are termed polymeric, an expression which is especially employed with regard to such compounds in which identical or similar atomic linking is assumed.

Where such isomerides appear possible, that is, where several forms of combination may exist, the second problem to be solved is, which of these forms of combination corresponds to the constitution of the given compound? by which of the possible formulæ is the nature of the combination to be expressed? This second problem is purely experimental, and can only be solved by experimental (chemical) means. The successful solution of this problem is often very difficult; in most cases it demands great caution, and generally assumes a rich empirical material, which can only be acquired by laborious investigations. But with every care and trouble, every consideration and precaution, the attempts to solve this problem have often led to delusions and errors, which were only removed, or have still to be removed, by renewed exertions. The solution of this problem has scarcely been attempted, to say nothing of its accomplishment, for a large number of compounds which have been both analysed and investigated. But if we remember that really effective investigations of this nature were first attempted half a century ago, and that they were for a long time regarded by many chemists with suspicion, as being too bold, we may be proud of the numerous results which have been acquired, and can look to the future with hope and confidence. If the words of the poet,

Ins Innere der Natur dringt kein erschaffener Geist,

are in any sense true, then the nature of the arrangement of the atoms belongs to the 'inner' nature of matter just as little as do the most distant objects in the universe of the condition and constituents of which we have been able to

gain information, although they only appear to our most powerful telescopes as feebly luminous points or nebulous spots.

§ 112. In many cases the solution of the first part of the problem, viz. the discovery of the possible forms of combination for a given composition, is simple and easy, but in some cases it is most difficult and complicated. The difficulty of its solution depends essentially on the chemical value and on the number of the atoms contained in the molecule. We will, therefore, consider the problem from both points of view. But it is unnecessary to investigate all the cases which are possible, since in many instances they cannot be applied to any known compounds. The cases will be chosen so that each may be illustrated by a concrete example. It will be seen that the number of examples of a given kind is often very small, so that in many cases they can be easily enumerated, whilst in other groups the space at our disposal no longer permits of their treatment in detail.

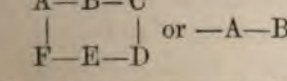
The constitution of compounds composed of monovalent elements is obvious. Since only two atoms can unite together, the structure of all these compounds is identical,

A—B which is identical with B—A,

since the sequence of the atoms cannot in this case give rise to any difference. Monovalent atoms cannot form compounds isomeric with each other.

In addition to the four compounds HF, HCl, HBr, HI, in the first division of the first table of § 90, p. 177, the only other compounds of monovalent atoms which are known are the molecules of the elements themselves, viz. HH, FF, ClCl, BrBr, II, and iodine chloride, ICl, and the compounds, IBr and BrCl, also probably belong to this class.

According to theory, compounds composed entirely of divalent elements must either form closed rings or contain two free affinities.



A different arrangement of the atoms, and also the fact of the chain being open or closed, appears to render the

existence of isomerides possible. In the small number of compounds of this description, which are capable of existing in the gaseous state, no cases of isomerism have yet been observed. If sulphur and selenium are, as many chemists assume, divalent in the compounds SO_2, SeO_2, and SO_3, then they form either ring-shaped or open chains. In the latter case each must contain two unsaturated affinities.

Some divalent elements, like Cd and Hg, occur in the isolated state as individual atoms, consequently with non-saturated affinities; others whose divalence is not beyond doubt form molecules of two or more atoms, *e.g.* oxygen O_2, ozone probably O_3, either united in a ring or as an open chain; sulphur at 500° C, *i.e.* near its boiling point, S_6, between 800° and 1000° S_2. Selenium above 1400° Se_2, at a somewhat lower temperature some particles at least are larger, probably Se_3 or Se_6. Compounds of divalent with monovalent elements can only exist as open, not branched chains: $\dot{a}$—$\ddot{A}$—$\ddot{B}$—$\ddot{C}$—$\ddot{D}$—$\dot{b}$, which can never contain more than two monovalent atoms (§ 101). This theoretical result is in accordance with experience, since no compound of this description is known to contain more than two monovalent atoms in the molecule.

No isomerides can exist of compounds containing only one description of divalent atoms.

Water, H—O—H
Hypochlorous oxide, Cl—O—Cl
Sulphuretted hydrogen, H—S—H
Seleniuretted hydrogen H—Se—H,
Telluretted hydrogen, H—Te—H.

According to theory no isomers can exist of compounds containing two dissimilar divalent and two similar monovalent atoms; *e.g.*

Thionylchloride, Cl—S—O—Cl
Selenylchloride, Cl—Se—O—Cl.

Cases of isomerism are possible as soon as the molecule contains more than two divalent atoms of two or more different species. It is doubtful, however, whether molecular weights of compounds of this composition have been determined. If the acid chlorides of sulphur belong to this class, then

isomerides of sulphuryl chloride, SO_2Cl_2, chlorosulphonic acid, SO_3HCl, pyrosulphuryl chloride, $S_2O_5Cl_2$, may exist. Their number can be easily calculated by permutations. Two compounds having the composition of sulphuryl chloride are possible :

Cl—O—S—O—Cl, and Cl—S—O—O—Cl.

Only one of these is known. It receives the first formula on account of its chemical properties. Four different arrangements of the atoms are possible in the case of chlorosulphonic acid.

Cl—O—O—O—S—H Cl—O—O—S—O—H
Cl—O—S—O—O—H Cl—S—O—O—O—H

Chemists who regard sulphur and oxygen as divalent assign the third of these formulæ to the only known compound having this composition. A compound, which differs from pyrosulphuryl chloride $S_2O_5Cl_2$, by containing two different monovalent atoms, *e.g.* one of bromine and one of chlorine, could form twenty-one different isomerides, $6+5+4+3+2+1=21$. But if both the monovalent atoms were alike, then nine pairs of these compounds would be identical, so that $21-9$, *i.e.* 12 different formulæ for pyrosulphuryl chloride are possible.

The only known compound of this composition has the constitutional formula Cl—O—S—O—O—O—S—O—Cl, as deduced from its mode of formation and chemical properties. The fact that none of the isomerides of these compounds are known to us renders the hypothesis of the divalence of sulphur and selenium doubtful.

§ 113. Strange to say, all the compounds of trivalent with monovalent elements, the molecular weights of which have been determined by Avogadro's law, contain only one atom of the trivalent element. These compounds are tabulated in § 90, under III. No compound in the gaseous state is known containing two or three kinds of monovalent elements combined with a trivalent element. All compounds of this group are, therefore, formed on the model $\begin{matrix} a \\ | \\ A \\ | \\ a \end{matrix}\!\!\begin{matrix} - \\ \\ - \\ \\ - \end{matrix}\!\!\begin{matrix} a \\ \\ a \\ \\ a \end{matrix}$ in which isomerism

is impossible.[1] The trivalent elements form some compounds with divalent elements, which differ in the atomic arrangement of their molecules: some of these compounds undoubtedly possess free affinities. The arrangement of the atoms in these compounds is often very doubtful, as different combinations appear possible in almost all cases. The investigation is rendered especially difficult by the doubt which reasonably exists as to whether the elements nitrogen, phosphorus, &c., which appear to be trivalent in their compounds with hydrogen, should also be regarded as trivalent in their oxygen compounds.

Nitrogen and oxygen form three compounds, the molecular weights of which can be determined, nitric oxide, NO, nitrous oxide, N_2O, and the so-called nitrogen di- or tetroxide; the molecular weight of the latter is represented by N_2O_4 at low temperatures, and NO_2 at higher temperatures. In the latter state this compound, like nitric oxide, contains one or more free affinities, since the sum of these affinities is uneven, for nitric oxide $3+2=5$, nitrogen tetroxide $3+2+2=7$. The molecular weight of nitrogen trioxide, which is hypothetically assumed to be N_2O_3, has not been and perhaps never will be determined.

If N is trivalent[2] these compounds have the following constitution.

Nitrous oxide $\begin{matrix} N=N \\ \diagdown\diagup \\ O \end{matrix}$

Nitric oxide $O=N-$*

Nitrogen peroxide at high temperatures $O=N-O-$*

Nitrous anhydride $O=N-O-N=O$

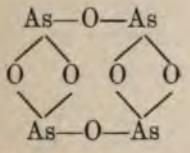
Nitrogen peroxide at low temperatures $O=N-O-O-N=O$

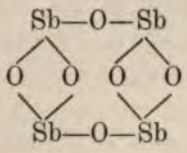
For nitrous oxide only one mode of arrangement of the atoms is possible, unless free affinities are assumed to exist in the molecule, and there is no reason for assuming this to be the case. At least one free affinity is contained in nitric oxide NO, and also in nitrogen peroxide at high temperatures. Unless this number of free affinities is unnecessarily assumed to be larger, then the constitution of NO given above is the

[1] See § 168.

[2] Another view of the constitution of these oxides will be discussed in Section IX. § 178.

only one possible. A second formula is possible for NO_2, in which the nitrogen would possess the free affinity. Several combinations are possible in the case of N_2O_3 and N_2O_4. The constitution given above is ascribed to them on account of the ease with which they are formed from, and are converted into, nitric oxide. Arsenious and antimonious oxides, As_4O_6 and Sb_4O_6,[1] the molecular weights of which are, as a rule, incorrectly given in textbooks as As_2O_3 and Sb_2O_3, may be represented by one of several structural formulæ. The most probable of these are



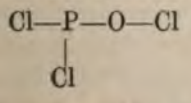


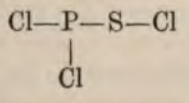
which exhibit perfect symmetry as regards the atoms of the metals.

But these oxides are isodimorphous, and arsenious oxide also occurs in a third amorphous modification. These different conditions probably correspond to three different constitutional formulæ.

Many compounds of determinable molecular weight are known which may be regarded as composed of tri-, di-, and mono-valent elements; *e.g.* the acid chlorides and bromides of nitrogen and phosphorus. But the molecular weights of only a few of these bodies have been determined, and these contain only a small number of atoms in the molecule. This is probably true of the other analogous compounds, the molecular weights of which have still to be determined.

The molecular weights of phosphorus oxychloride, $POCl_3$, and phosphorus thiochloride, $PSCl_3$, have been determined. The constitutional formulæ of these bodies are





Phosphorus oxybromide, $POBr_3$, and phosphorus oxychlorobromide, $POCl_2Br$, are considered to have analogous constitu-

[1] V. and C. Meyer, *Ber. d. deut. chem. Ges.* 1879, 1282.

tions and analogous molecular weights. Isomerides could only exist in the case of the last compound, according as Cl or Br is united with O; but such isomerides are not known.

In their experiments on the vapour density of nitric acid, Wanklyn and Playfair [1] found numbers which were somewhat higher than the molecular weight $HNO_3 = 62{\cdot}9$.

This cannot arise from a partial decomposition of the acid, since the products of decomposition would occupy a larger and not a smaller volume than the vapour of the undecomposed acid. The only explanation which remains is that a small portion of the acid has a larger molecular weight, $H_2N_2O_6 = 125{\cdot}8$, for example. If nitrogen is trivalent, the molecular weight HNO_3 can be represented as

$$O=N-O-O-H, \text{ or } \begin{matrix} O \\ | \\ O \end{matrix}\!\!\diagdown\!\!\diagup N-O-H.$$

The molecular weights of some of the five oxychlorides and oxybromides of nitrogen have been indirectly determined, and others are still undetermined. But in all probability they correspond to the formulæ,

$$NOCl\,.\,NOCl_2\,.\,NOBr\,.\,NOBr_2\,.\,NOBr_3$$

The second and fourth of these formulæ exhibit free affinities, the fifth is analogous to phosphorus oxychloride. The first and third formulæ are connected with the preceding constitutional formulæ for nitric oxide and its derivatives; *e.g.*

$$O=N-Cl, \text{ and } O=N-Br,$$

which easily explains the formation of these compounds from nitric oxide, as observed by Gay-Lussac [1] and Landolt.[2]

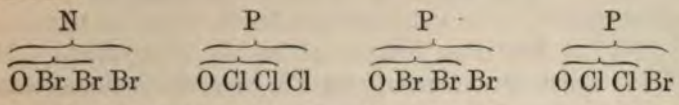
The investigation of the constitution of the oxychlorides and bromides of nitrogen and phosphorus possesses a special interest at present, as many chemists regard the nitrogen and phosphorus atoms in these compounds as pentavalent. In this case these elements do not belong to the third but to the fifth group, the group of pentavalent elements. According to this

[1] *Proc. Soc. Roy. Edin.* 1861, iv. 395; Kopp and Will, *Jahresber.* 1861, xiv. 23.

[2] *Ann. Chim. Phys.* [3] 1848, xxiii. 203.

[3] *Lieb. Ann.* 1860, cxvi. 177.

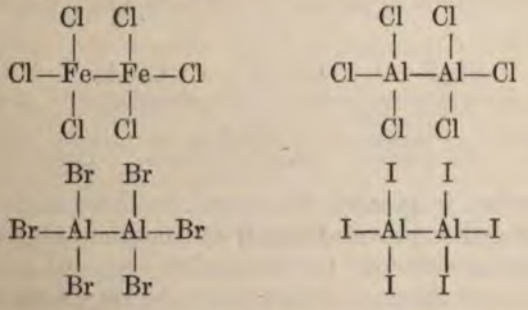
view, they would be represented by the following structural formulæ :



This subject will be discussed in Section IX.

§ 114. The molecular weights of a very large number of compounds containing tetravalent elements have been determined. The large number and the diversity of the compounds is essentially due to those of carbon, as this element is distinguished from all others by the great tendency of its atoms to unite with one another forming long and complicated series.

If the carbon compounds are not taken into account, the number of the compounds of the tetravalent elements which are known in the gaseous state is not large. The compounds in column IV. of the table § 90, which are composed of one tetravalent and four monovalent atoms, belong to this class. To these may be added ferric chloride and aluminium chloride, bromide and iodide which contain two tetravalent atoms in the molecule. The constitution of these compounds is represented by the following formulæ :



No other arrangement of two polyvalent and six monovalent atoms is possible. It is, however, questionable whether Al and Fe are really tetravalent.

§ 115. With the exception of the small number of cases mentioned in the preceding paragraphs, our knowledge of atomic linking and of the constitution of compounds is confined exclusively to the numerous carbon compounds, which

daily increase in number. The constitution of the large majority of these compounds has still to be investigated. The methods employed in the investigation of atomic linking have arisen from the investigation of carbon compounds. The methods which were formerly used to investigate the so-called 'organic radicals' have been developed, and are now directed towards a clearly defined goal. The radicals are now recognised as atomic chains separated from a compound.

For compounds of carbon with different monovalent elements the following equation holds: $n_1 \leqq 2n_4+2$.

The problem is the simplest when neither free affinities nor double linkings of the carbon atoms occur. This is the case when $n_1 = 2n_4+2$, that is, when the compound contains the maximum number of monovalent atoms, which is two more than double the number of C atoms.

This will be the first case for investigation.

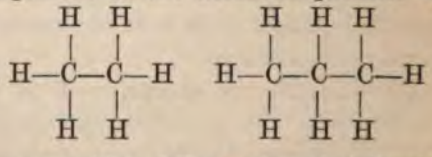
When $n_4 = 1$ and consequently $n_1 = 4$, no cases of isomerism are possible, unless we assume that the four units of affinity of one and the same carbon atom differ from each other. At present there are no sufficient grounds for this assumption. No isomers are known of this class of compounds, whether they contain one or more kinds of monovalent atoms; *e.g.*

CH_4	CH_3F	CH_3Cl	CH_3Br	CH_3I
Marsh gas.	Methylfluoride.	Methyl chloride.	Methyl bromide.	Methyl iodide.

$CHCl_3$	$CHBr_3$	CH_2Cl_2	CCl_4
Chloroform.	Bromoform.	Methylene chloride.	Carbon tetrachloride.

Isomerism is possible when two or three carbon atoms combine together, provided that the monovalent atoms are not all of the same element; it is impossible when the monovalent atoms are all of the same description, as hydrogen, for example. Only one mode of arrangement of the atoms is possible for the compounds:

C_2H_6[1] and C_3H_8, viz.



[1] Two hydrocarbons of the compositions C_2H_6 were formerly believed to exist—one formed from C_2H_5 and H, the other from CH_3 and CH_3. The

or, to use more simple formulæ,

$$H_3C—CH_3 \text{ and } H_3C—CH_2—CH_3.$$

The existence of isomerides of the second of these compounds is possible, as soon as a single atom of a different monovalent element, *e.g.* chlorine, replaces one of the hydrogen atoms. In the first of these compounds, however, it is quite clear that both the carbon atoms occupy similar positions, and it is quite immaterial whether the chlorine atom is attached to the first or to the second atom of carbon. But in compounds in which three carbon atoms are linked together the position of the middle C atom differs from that of the end atoms. Consequently two different compounds can be formed when an atom of hydrogen is replaced by a chlorine atom. These are not identical but merely isomeric:

$$H_3C—CH_2—CH_2Cl \text{ and } H_3C—CHCl—CH_3.$$

In the case of the hydrocarbon containing two carbon atoms, isomerism is only possible when two atoms of hydrogen are substituted by chlorine; *e.g.*

$$H_3C—CHCl_2 \text{ and } ClH_2C—CH_2Cl.$$

Two different substances can also be produced by a further substitution of chlorine for hydrogen, $H_2ClC—CCl_3$, and $HCl_2C—CHCl_2$.

But the possibility of isomeric compounds now ceases, since there is only one form for the composition $HCl_2C—CCl_3$, and of the final product, carbon sesquichloride $Cl_3C—CCl_3$.

The results of observation exhibit complete agreement with the deductions from theory; in accordance with theory only one compound, C_2H_6, is known, one C_2H_5Cl, two $C_2H_4Cl_2$, two $C_2H_3Cl_3$, two $C_2H_2Cl_4$, one C_2HCl_5, and one C_2Cl_6.

If the compound contains three or more different kinds of monovalent atoms, then it is possible to have more than two isomeric compounds. The number of possible isomerides can easily be calculated. Assuming that all the monovalent atoms

former was called ethyl hydride and the latter dimethyl. The identity of these bodies was proved by C. Schorlemmer (*Ann. Chem. Pharm.* 1864, cxxxi. 76; cxxxii. 234).

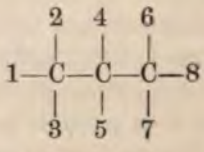
are of different kinds, and distinguishing them by the numbers 1 to 6, then the following combinations will be possible :

Attached to the first C atom	Attached to the first C atom	Attached to the second C atom	Attached to the second C atom
1, 2, 3	1, 3, 5	4, 5, 6	2, 4, 6
1, 2, 4	1, 3, 6	3, 5, 6	2, 4, 5
1, 2, 5	1, 4, 5	3, 4, 6	2, 3, 6
1, 2, 6	1, 4, 6	3, 4, 5	2, 3, 5
1, 3, 4	1, 5, 6	2, 5, 6	2, 3, 4

The number of possible combinations is $\frac{1}{2}\frac{6 \cdot 5 \cdot 4}{1 \cdot 2 \cdot 3} = 10.$

If two of the six monovalent atoms are of the same description, three of these ten combinations will be identical with the other three, so that the number of possible isomeric compounds is diminished by three. It is clear that if three of the atoms are alike, the number will be diminished by six; and if four are alike, it will be diminished by eight; so that only two isomeric compounds are possible, as was shown above.

§ 116. It has been previously stated that when three carbon atoms are linked together no isomeric compounds are possible so long as the monovalent atoms are all of the same nature. Only one single compound can exist which is composed of three similar tetravalent and eight similar monovalent atoms. But if the eight monovalent atoms were all different, there are, according to the rules of combinations, no less than 280 forms of combination according to the manner in which these atoms are united to the three similar tetravalent atoms. No less than 280 different isomeric compounds can exist, all of which have a structure similar to the following :



This is obvious, when it is remembered that the two affinities 4, 5 of the central carbon atom can be occupied by twenty-eight different combinations of two of the eight monovalent atoms $7 + 6 + 5 + 4 + 3 + 2 + 1 = 28$.

In each of these twenty-eight different arrangements, the remaining six atoms may be combined in ten different forms, as was shown in the preceding paragraph.

In reality such a dreadful multiplicity of compounds does not appear to be possible, since only four different kinds of monovalent atoms are known possessing the power of replacing the hydrogen in hydrocarbons. Including hydrogen, there are therefore five different kinds of monovalent atoms: hydrogen, chlorine, bromine, iodine, and fluorine. These elements would be able to form a very large number of isomeric compounds with three atoms of carbon. At present only a very small number of compounds of carbon with more than two kinds of monovalent elements have been prepared, so that it is unnecessary to enter into theoretical considerations of such compounds. Our speculations will be confined to compounds containing only two kinds of monovalent elements, as hydrogen and chlorine, for example.

When an atom of hydrogen in C_3H_8 is substituted by an atom of chlorine, two isomeric compounds may be formed, since the chlorine may combine with the middle or one of the end carbon atoms.

A. $CH_3—CHCl—CH_3$, or *B*. $CH_3—CH_2—CH_2Cl$.

By the addition of a second chlorine atom to either of these substitution products, two new substitution products containing two atoms of chlorine may be derived from the first (*A*) and three from the second (*B*) of these chlorides. But one of the products from *A* is identical with one of the products from *B*. Four isomeric compounds $C_3H_6Cl_2$ are therefore possible.

$CH_3—CHCl—CH_2Cl$ $\quad$ $CH_3—CH_2—CHCl_2$

$CH_3—CCl_2—CH_3$ $\quad$ $CH_2Cl—CH_2—CH_2Cl$.

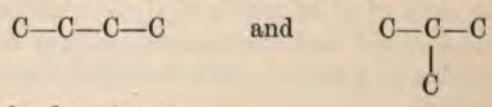
It is also obvious that five different isomeric compounds of the composition $C_3H_5Cl_3$ may exist, and six compounds having the formula $C_3H_4Cl_4$. The number of isomerides decreases in the same way as it increased, when the number of chlorine atoms is increased at the expense of the hydrogen.

The following thirty compounds of three carbon atoms with eight chlorine or hydrogen atoms may exist:

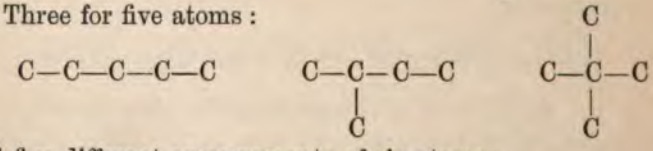
C_3H_8	1 compound.	$C_3H_3Cl_5$	5 compounds.
C_3H_7Cl	2 compounds.	$C_3H_2Cl_6$	4 ,,
$C_3H_6Cl_2$	4 ,,	C_3HCl_7	2 ,,
$C_3H_5Cl_3$	5 ,,	C_3Cl_8	1 compound.
$C_3H_4Cl_4$	6 ,,		

Whether all these compounds can be produced by the action of chlorine on the hydrocarbon C_3H_8 cannot at present be ascertained.

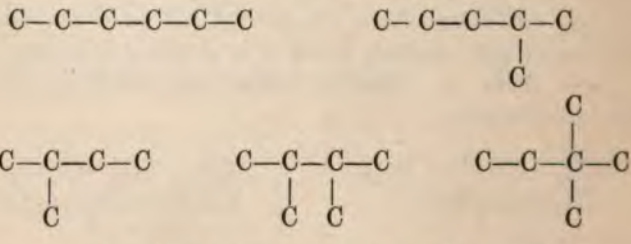
§ 117. This large number of compounds is greatly increased as soon as different arrangements of the carbon atoms are possible. This occurs when four or more carbon atoms are linked together in a compound, as the formation of one or more side chains then becomes possible. Two kinds of linking are possible for four carbon atoms; *e.g.*



Three for five atoms:



and five different arrangements of six atoms:



There are nine different arrangements of seven atoms, and eighteen of eight atoms, &c.

In all these different systems of atoms $2n_4 + 2$ affinities, which are not used in linking the carbon atoms together, are available for combination with other atoms, so that an aston-

ishingly large number of compounds is possible, even when the $2n_4 + 2$ affinities are merely satisfied by monovalent atoms.

The existence of isomerides of this description was predicted by Kolbe [1] on theoretical grounds before the existence of any of these compounds had been proved. Kolbe started with the idea that by the substitution of CH_3, or an analogous radical, for H in a compound of the formula CH_3—X, for example, CH_3 . OH, a single body would be produced, CH_3 . CH_2—X. This latter would yield two substitution products,

$$CH_3—CH_2—CH_2—X \quad \text{and} \quad CH_3—\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}—X$$

from which three derivatives could be obtained, and so on.

$$CH_3—CH_2—CH_2—CH_2—X \quad CH_3—CH_2—\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}—X \quad CH_3—\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{\displaystyle |}{\overset{\displaystyle |}{C}}}}—X$$

After these predictions of Kolbe's had been confirmed by experience he advanced further speculations, which, however, require further confirmation.[2]

While it is generally agreed that the great difference in the behaviour of two hydrogen groups in a compound CH_3—CH_2—X, for example, CH_3—CH_2—OH, is caused by the vicinity of X, OH, &c., Kolbe attributes the cause to the opposite properties of the carbon atoms. According to his hypothesis two methyl groups (CH_3) can unite in two different ways, according as they are equally 'co-ordinated,' or one is 'subordinated' to the other, so that two hydrocarbons of the composition C_2H_6 are possible. Their composition is represented by Kolbe by the formulæ [3]

$$CH_3—CH_3 \qquad \text{and} \qquad \left.\begin{matrix} CH_3 \\ H_3 \end{matrix}\right\} C$$

Dimethyl. Methylated methane.

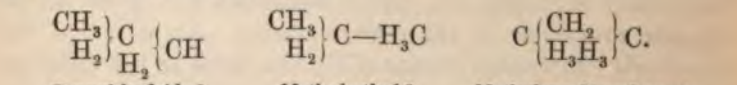
[1] Kolbe, *Ausf. Lehrb. d. org. Chemie*, i. 567 (written in 1858); *Lieb. Ann* 1860, cxiii. 305; *Zeitschr. Chem. Pharm.* 1862, 687.

[2] See several articles in the *Journ. f. prak. Chemie*, also his *Kurz. Lehrb. d. org. Chemie.*

[3] *Kurz. Lehrb. d. org. Chemie*, Braunschweig, 1879, p. 84.

The first is regarded as formed by the union of two methyl (CH_3) radicals, the second by the substitution of methyl (CH_3) for an atom of hydrogen in marsh gas or methane, in which the three other hydrogen atoms retain their typical character, which is not possessed by the three new atoms (see § 99). This is expressed in the second formula by placing the substituted CH_3 (which is regarded as subordinate to the other), and the three original typical hydrogen atoms before the bracket, but the chief carbon atom is placed after the bracket. Where the difference exists between these two kinds of compounds, why one atomic group is more important than the other similar group is only slightly hinted at by Kolbe. He believes that the four hydrogen atoms of methane are united to the carbon atom by affinities of different strengths.[1]

If it is assumed that all the four affinities of carbon are dissimilar, then it is clear that two atoms could unite in $4 + 3 + 2 + 1 = 10$ different ways; $3 + 2 + 1 = 6$ compounds if there are three kinds of affinities, and $2 + 1 = 3$ compounds for two sorts of affinities, and only one compound when all the affinities are alike. According to this hypothesis therefore more than two methods of combination are possible. But assuming only two kinds of combination be possible, a much larger number of isomerides can exist than as stated in §§ 115–117. For example, there would be a whole series of isomeric propanes, C_3H_8, such as;



Propyl hydride.[2] Methyl ethyl.[2] Methylene dimethane.[3]

If these predictions of Kolbe's are confirmed by experiment, as others of his have been, an enormous number of isomeric compounds may exist. Their number would even be larger than the author of these speculations expected. Kolbe does not even state whether the mode of combination termed 'co-ordination' is possible in the radicals as well as in the hydrocarbons. Should this be so several new isomeric alcohols and

[1] See the introduction to the section 'Aromatische Verbindungen,' p. 370 in the book mentioned in the preceding note.

[2] *Kurzes Lehrb.* p. 193. [3] *Journ. f. prak. Chemie*, 1880, xxii. 157

acids might exist, for instance, different normal primary alcohols (normal butyl carbinol), *i.e.* compounds of the composition $C_5H_{11}OH$, with straight non-bifurcated chains. But when the carbon atoms are supposed to be of the same value, only one such compound is possible, $CH_3—CH_2—CH_2—CH_2—CH_2—OH$, and even according to Kolbe [1] only one can exist, having the formula

$$\begin{matrix} CH_3 \\ H_2 \end{matrix}\Big\{C\Big\{\begin{matrix} C \\ H_2 \end{matrix}\Big\{\begin{matrix} C \\ H_2 \end{matrix}\Big\{\begin{matrix} C \\ H_2 \end{matrix}\Big\{COH.$$

In our present state of knowledge the question of the similarity or dissimilarity of the different affinities of a polyvalent atom is without doubt an open question. It is therefore permissible to assume that they are dissimilar.

Some facts which will be discussed in Section IX., § 168, can be most easily explained by the assumption of such a dissimilarity, although they are capable of another explanation. Until the thousands of organic compounds exhibit more cases of isomerism than are predicted by the simple hypothesis which forms the basis of the chain formulæ, it is permissible, if not obligatory, to adhere to this hypothesis until the results of observation render it necessary to turn to the less simple assumption of the dissimilar affinities of polyvalent atoms. That this extension of the theory would be accomplished without difficulty, is seen from the similarity of the formulæ used above to illustrate both systems.

§ 118. When the number of monovalent atoms in the compound does not reach its maximum, and $n < 2n_4 + 2$, the number of possible isomerides is still greater, independently of whether it is due to free affinities or to double linking of the carbon atoms.

In the case of unsaturated affinities the number of isomeric compounds possible is as large as it would be if the same number of affinities were saturated by a particular monovalent atom. For example, the number of possible compounds C_nH_{2n} with two free affinities is the same as the number of compounds of the composition $C_nH_{2n}Cl_2$, or, to make use

[1] *Kurzes Lehrbuch*, p. 242.

of a general expression, the number of possible compounds of the formula C_nH_{2n+2-x} is equal to the number of compounds $C_nH_{2n+2-x}Cl_x$, which are theoretically capable of existence.

In cases of the double linking of the carbon atoms the number is somewhat smaller, since the affinities which are mutually linked together cannot both belong to the same atom. According to the views of many chemists one atom cannot possess two unsaturated affinities simultaneously. But this is obviously true in the case of the carbon atom in carbon monoxide, and also of the atoms in the vapours of mercury and cadmium. The existence of exceptions to this rule can be proved with certainty, but it is difficult to establish the validity of the rule itself. Assuming the existence of free affinities, two compounds of the composition C_2H_4 are possible,

$$*H_2C—CH_2* \quad \text{and} \quad H_3C—CH**$$

but with double linking only one can exist, $H_2C = CH_2$.

Only one compound C_2H_4 is known, viz. ethylene. As all attempts to prepare the isomeride ethylidene have failed, this appears to indicate that the carbon atoms in ethylene are united by double linking, and do not possess free affinities.

§ 119. The compounds of carbon with divalent atoms are not nearly so numerous as those with monovalent. The carbonates and oxalates of the divalent metals belong to this class, but their molecular weight cannot be directly determined. The molecular weight of the following easily volatile compounds is known:

CO, carbon monoxide.	CO_2, carbonic anhydride.
COS, carbonyl sulphide.	CS_2, carbon bisulphide.

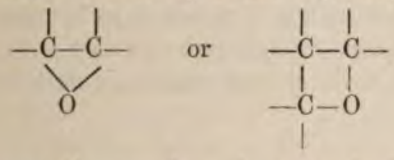
In carbon monoxide two of the affinities of the tetravalent carbon are unsaturated. In the three other compounds the affinities of the two divalent atoms just suffice to saturate those of the tetravalent atom.

It may be remarked that, although compounds of carbon with a large number of divalent atoms are theoretically possible (since the latter may unite with each other, forming a very long chain), no compounds of this description have been prepared.

A very large number of carbon compounds contain both mono- and di-valent atoms. The divalent atoms may be arranged in different ways; *e.g.*

1. The divalent atom oxygen, for example, saturates two affinities of one and the same atom: $O = C =$

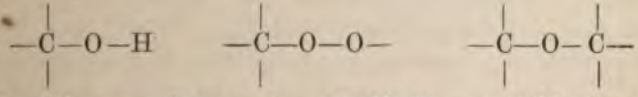
2. It is attached by its affinities to two carbon atoms which are directly or indirectly linked together,



In both cases the number of monovalent atoms which might have been contained in the compound is diminished by two for each divalent atom. In this case

$$n_1 \leq 2n_4 - 2n_2 + 2.$$

3. The divalent atom unites two other atoms together, which are otherwise neither directly nor indirectly combined; *e.g.*



In this case the number of affinities available for union with monovalent atoms is not diminished by the introduction of divalent atoms; therefore

$$n_1 \leq 2n_4 + 2;$$

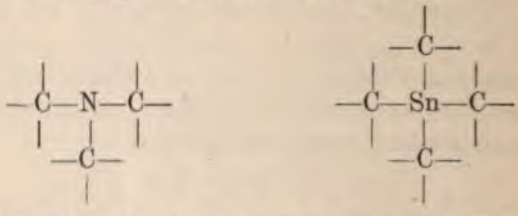
i.e. the number of monovalent atoms is independent of the divalent atoms.

§ 120. The different cases presented when trivalent atoms occur in the compound will be easily understood from the following general formulæ:

1. $N \equiv C -$ $\qquad n_1 = 2n_4 - 3n_3 + 2.$
2. $-N = C =$
3. $= C - C =$ (N—) $\qquad n_1 = 2n_4 - n_3 + 2.$
4. $= N - C =$ $\qquad n_1 = 2n_4 + n_3 + 2.$

It is immaterial whether the free affinities of the tri- and tetra-valent atoms are satisfied by mono- or di-valent atoms; in the latter case the rules laid down in the preceding § generally hold good. When tetravalent atoms of other elements combine with carbon the same forms of combination are produced as when the carbon atoms themselves combine.

It more frequently happens with such tri- and tetra-valent atoms than with carbon, that one atom is united to carbon by each of its affinities, forming in this way a nucleus or central point to which three or four chains are united:



In addition to the above cases numerous compounds are known in which the affinities of the atom united to the carbon are partly saturated by monovalent or divalent atoms. In the latter case the compounds formed are generally non-volatile, and consequently the molecular weights are as a rule not known.

§ 121. Only a few compounds exist which undoubtedly contain pentavalent elements, whose molecular weights are known. Only one single hexavalent compound is known, viz., the compound mentioned in § 90, under V. and VI. Multiple linkings amongst these elements are unknown. On account of their rarity these types are of less importance than the first four types, which will be discussed in detail in the following pages.

§ 122. The theoretical investigation of the possible forms of combination which has been described in its chief features in the preceding paragraphs, is only capable of deciding the arrangement of the atoms in a given compound, in one case, viz. when the atoms which analysis has shown to exist in the molecule of the compound can only be arranged in one form. For example, the arrangement of the atoms in, or, to use the usual expression, the constitution or structure of such compounds as, CH_4, CH_3Cl, C_2H_6, C_2H_5Cl, C_3H_8, &c., is perfectly

clear, if the hypotheses are recognised which form the basis of the theory of atomic linking.

The formulæ of these compounds only admit of one interpretation. On the other hand, the theoretical consideration of the combinations possible has shown the inadmissibility of many of the constitutional formulæ, proposed in former times for different substances, which at the time were regarded as correct. This is true of almost all the hypotheses in the so-called 'etherine theory'[1] first propounded by Gay-Lussac and afterwards developed and supported by Dumas. According to this theory a whole series of compounds of carbon contains the group C_4H_8 (termed 'etherine' by Berzelius[2]) in combination with other atomic groups. This group of atoms which is now halved and called ethylene does indeed contain two free affinities according to our present views:

$$n_4 = 4, \text{ and } n_1 = 8, \text{ therefore } n_1 < 2n_4 + 2 = 10.$$

But most of the atomic groups with which etherine was supposed to combine would require the whole of the affinities of the atoms contained in them, to preserve the coherence of their molecules. They have consequently no affinities left by which they can unite with ethylene. This is easily seen from the following examples. According to the etherine theory

Ethyl chloride is	$C_4\overline{H}_4$, $\overline{H}Cl$	or	C_4H_8, HClHCl
Ether	$C_4\overline{H}_4$, $\overline{H}O$	,,	C_4H_8, H_2O
Alcohol	$C_4\overline{H}_4$, $\overline{H}O$, $\overline{H}O$	,,	C_4H_8, H_2O, H_2O
Ethyl sulphide	$C_4\overline{H}_4$, $\overline{H}S$	,,	C_4H_8, H_2S
Mercaptan	$C_4\overline{H}_4$, $\overline{H}S$, $\overline{H}S$	,,	C_4H_8, H_2S, H_2S

H—Cl, H—O—H, H—S—H are closed groups, and do not possess any free affinities enabling them to combine either with each other or with etherine.

The 'ethyl theory' of Berzelius and Liebig[3] is more in accordance with our present views. In accordance with this theory also, though to a smaller extent, compounds were

[1] The history of this theory is described by Ladenburg, *Vorträge über die Entwickelungsgeschichte der Chemie*, p. 129.

[2] Berzelius, *Jahresber.* No. xii. 303; No. xiii. 192, 197.

[3] Ladenburg, *loc. cit.* p. 138; Berzelius, *Jahresber.* No. xiii. 196.

represented as formed by the union of atomic groups not possessing free affinities.

According to this theory

Ethyl chloride is	C_4H_5, Cl	or	C_4H_{10}, Cl_2
Ether	C_4H_5, O	,,	C_4H_{10}, O
Alcohol	C_4H_5, O, HO	,,	C_4H_{10}, O, H_2O
Ethyl sulphide	C_4H_5, S	,,	C_4H_{10}, S
Mercaptan	C_4H_5, S, HS	,,	C_4H_{10}, S, H_2S

The formulæ for ether and ethyl sulphide are almost identical with those at present in use; in the other formulæ the groups which have no free affinities, such as H—O—H and H—S—H, do not occur twice, as is the case in the etherine theory. The occurrence of such groups forms one of the chief distinctions between the old theories and the present theory of atomic linking. It was formerly believed that any given group of atoms under suitable conditions possessed the power of combining with new atoms without losing any of the atoms previously contained in it. This power is, at the present time, only ascribed to those groups of atoms which conform to the equation (§ 106),

$$n_1 < n_3 + 2n_4 + 2.$$

Whilst, those satisfying the conditions of the equation,

$$n_1 = n_3 + 2n_4 + 2$$

are considered as lacking this ability. But the latter equation is valid in the case of almost all the atomic groups of the old ethyl theory, thus:

C_4H_{10}	$n_1 = 10 = 2n_4 + 2$	H_2O	$n_1 = 2$
$C_4H_{10}O$	,, ,, ,,	H_2S	,,
$C_4H_{10}S$	,, ,, ,,	Cl_2	,,

These atomic groups have not the properties of radicals; they do not possess any available affinities, at any rate, not such as would bring about and maintain the union of the atoms in the molecules of gaseous bodies. Whether such atomic groups can be accepted as constituents of liquid or solid substances will be discussed in another chapter. To regard these groups as constituents of compounds which

volatilise without decomposition is to completely ignore the information as to the mode of action of chemical affinity, which has been recently acquired. It is therefore not permissible to regard the so-called hydrate of a volatile acid as a compound of water and the anhydrous acid, alcohol as a compound of ether and water, an ethereal salt as a compound of an anhydrous acid and ether; *e.g.*

Acetic acid .	$\overline{H}\,O, C_4\overline{H}_3O_3$	or	$H_2O, C_4H_6O_3$
Alcohol . .	$\overline{H}\,O, C_4\overline{H}_5O$	,,	$H_2O, C_4H_{10}O$
Acetic ether	$C_4\overline{H}_5O, C_4\overline{H}_3O_3$	,,	$C_4H_{10}O, C_4H_6O_3$

These and similar constitutional formulæ are called 'dualistic,' as they assume the existence of two (or more) closed groups of atoms in most compounds. They are now regarded as untenable, and have been replaced by the so-called unitary formulæ. At first sight there appears to be a wide difference between these formulæ, but in reality the difference is not very great, since the new formulæ retain everything in the old adapted to express the properties of the substances. Formerly those compounds which easily form water were supposed to contain water, H_2O, ready formed, but according to the present view they only contain the atomic group H—O—× hydroxyl, which easily takes up an atom of hydrogen and forms water; *e.g.*

	Dualistic	Unitary
Alcohol . .	C_4H_{10}, O, H_2O	$CH_3—CH_2—O—H$
Ether . .	$C_4H_{10}O$	$CH_3—CH_2—O—CH_2—CH_3$
Acetic acid .	C_4H_6, O_3, H_2O	$CH_3—CO—O—H$
Ethyl acetate	C_4H_6,O_5,C_4H_{10},O	$CH_3—CO—O—CH_2—CH_3$

The old idea that the so-called acid hydrates are compounds of anhydrous acids and water, and that salts are compounds of metallic oxides and acids, is not in unison with modern theories. Davy's latest theory of the hydrogen acids resembles the present one. Davy regarded an acid as composed of two parts, viz. the hydrogen which is replaceable by metals, and opposed to this as a whole the remaining atoms contained in the compound. According to our present view an acid is regarded simply as a group of atoms linked together. The modern

doctrine, whilst retaining the essentials of Davy's theory, has added greatly to it.

Gerhardt's system of types which followed the so-called electro-chemical system, founded on the dualistic hypothesis, contained a few radicals possessing no affinities available for combination with other atoms. After the discovery of the law of atomic linking these radicals were discarded. That the theory of types was not in a position to overthrow dualism is easily understood, since the theory itself was not quite free from some of the most vital errors of dualism; nor was it able to overcome the dualistic system until it had gained uniformity by the hypothesis of atomic linking.

§ 123. The critical negation of dualism and of other views opposed to the theory of atomic linking is a natural result of the theoretical speculations on the possible arrangement of the atoms; it requires no further experimental support. It possesses the same empirical foundation as the hypothesis of atomic linking, which is based on some thousands of observations.

The theoretical development of the deductions from this hypothesis also suffices for the determination of atomic linking in those compounds of known composition and known molecular weight, in which the atoms can according to theory be arranged in only one form.

But where several isomeric compounds can exist for a given molecular composition, the theoretical speculation is merely preliminary. The decision can only be arrived at experimentally, as has been already stated in § 111.

We will now describe the most important methods used for ascertaining the atomic linking. These methods are based on the knowledge of the formation and decomposition of the chemical compounds, and also on the knowledge of other chemical and physical properties.

The first step in the inquiry as to which of several possible isomerides is under investigation, consists in splitting up the chain of atoms of which it is composed into several pieces, in order to build it up again from the same fragments. It is assumed, first, that atoms which are liberated in the form of a connected chain, on the decomposition of a compound, existed

in direct union with each other in this compound; and, secondly, that, as a rule, when a connected chain of atoms passes from one compound to another, no alteration takes place in the order of the atoms. Further, when an atom or chain of atoms is expelled from a compound, and another atom or atomic chain with the same number of available affinities at the same time enters the compound, it is assumed that, as a rule, the combining portion takes the place of the expelled atoms, and does not replace other portions of the original compound. These assumptions do not always prove correct; in many cases they are clearly fallacious. But there are means of testing their accuracy by investigating the relation between the properties of the compound and its internal structure. This second method of investigation is equally as effective as the first. It is beyond doubt a correct principle that the same or similar properties are associated with similar or identical structure; or, in other words, like effects are produced by like causes. During the course of the present century, and more especially during the last forty years, the endeavour to investigate the mutual relations between composition and properties of bodies has opened out new fields of research, before undreamt of, which now form a wide neutral territory between the sister sciences of chemistry and physics. Nevertheless, the first stage in this extensive and laborious but fruitful field of investigation has scarcely been reached.

The methods which are in use in the investigation of atomic linking have been applied almost exclusively to the carbon compounds, and have been developed with special reference to these bodies. The large number of these compounds, the frequent occurrence of isomerides, necessarily fostered the development of these methods, without which a systematic survey of the well-known carbon compounds would scarcely appear possible. Any attempt to give an approximately complete account of the present use of these methods would, in spite of their incomplete development, far exceed the limits of this work. We shall therefore confine ourselves to illustrating the nature of these methods by a few examples.

§ 124. The application of the first method, viz. the splitting up and building together again of the atomic chains, consists

in attempting to decompose the compound of unknown constitution into substances of known constitution, and then building together the original compound from these fragments.

But in order to gain a complete idea of the whole chain of atoms, and to thoroughly understand their arrangement, a large number of different decompositions and formations of the substance must be known. The chain must be separated at different points, and built together again from the different fragments into which it was decomposed. A very extensive experimental investigation is generally necessary before the constitution can be ascertained with certainty. The atomic constitution can only be definitely settled when the investigation has been thus completely carried out.

Special weight is attached to rebuilding the chain from its isolated members. The rebuilding of the compound is termed a 'synthesis in the strictest sense,' when the two chains are united together by two carbon atoms.

Alcohol may be taken as an illustration of this method. Analysis and vapour density determinations show that its molecular formula is C_2H_6O. Two different modes of combining these atoms are possible, *e.g.* $CH_3—CH_2—OH$ and $CH_3—O—CH_3$. In fact, two isomeric compounds, alcohol and methyl ether, exist having this composition. The choice in this case is not difficult. The first compound contains one atom of H in a different position from the others. It is combined with oxygen to form hydroxyl, H—O—. The first formula is assigned to alcohol, because one of its hydrogen atoms exhibits different properties from the others; it is easily replaced by metals, like sodium, which have a great tendency to unite with oxygen, thus;

$$\underset{\text{Alcohol.}}{2(C_2H_5,OH)} + Na_2 = \underset{\text{Sodium alcoholate.}}{2(C_2H_5ONa)} + H_2.$$

In many reactions this atom of hydrogen is expelled, together with the oxygen atom; *e.g.*

$$\underset{\text{Alcohol.}}{C_2H_6O} + \underset{\text{Hydrochloric acid.}}{HCl} = \underset{\text{Ethyl chloride.}}{C_2H_5Cl} + \underset{\text{Water.}}{HOH}.$$

The formula for ethyl chloride, the compound formed in

the last reaction, only admits of one interpretation. According to theory, it has the composition $H_3C—CH_2—Cl$, and is, as Schorlemmer [1] has shown, not isomeric, but identical with the product obtained by the substitution of Cl for H in the hydrocarbon C_2H_6.

Since ethyl chloride is formed from alcohol by replacing OH by Cl, it is assumed that the hydroxyl occupied the position which the chlorine atom has taken, and therefore the arrangement of the atoms in alcohol may be represented by the formula $H_3C—CH_2—O—H$.

The action of hydrochloric acid on alcohol will then take place thus:

$$H_3C—CH_2—O—H + H—Cl = H_3C—CH_2—Cl + H—O—H.$$

If this arrangement of the atoms is accepted for alcohol, then the second formula is the only remaining possible formula for its isomeride methyl ether. The carbon atoms are not directly linked together, but are indirectly united by means of the oxygen atom. Its properties show that its atoms are really arranged in this order. The chain of atoms is difficult to split up, but it is easily built up from its members. Methyl ether is formed from methyl alcohol by several different reactions; the latter has no isomerides, its formula only admitting of one interpretation. Potassium methylate, $CH_3—O—K$, is formed by the action of potassium on methyl alcohol, $CH_3—O—H$. Methyl iodide is prepared by the action of hydriodic acid, HI, on methyl alcohol.

$CH_3—O—H$	+	HI	=	CH_3I	+	$H—O—H$.
Methyl alcohol.		Hydriodic acid.		Methyl iodide.		Water.

Methyl iodide acts on potassium methylate, according to the equation,

$CH_3—O—K$	+	CH_3I	=	$CH_3—O—CH_3$	+	KI.
Potassium methylate.		Methyl iodide.		Methyl ether.		Potassium iodide.

Methyl ether is therefore composed of two methyl groups, CH_3, which are united together by the atom of oxygen of

[1] C. Schorlemmer, *Ann. Chem. Pharm.* 1864, cxxxi. 76; cxxxii. 234.

the hydroxyl of the methyl alcohol. These and similar double decompositions confirm the correctness of the assumptions concerning the constitution of methyl ether, and also indirectly confirm the accuracy of the formula for alcohol.

§ 125. To ascertain the constitution of acetic acid having the composition $C_2H_4O_2$ is a somewhat more complicated problem. This compound either contains two free affinities or double linking of the atoms, since $n_1 = 4$ and $2n_4 + 2 = 6$. The existence of some thirty isomerides is by this circumstance rendered theoretically possible. But as one atom never enters into the molecule of acetic acid without another being expelled, it is probable that free affinities do not exist, and therefore the possibility of double linking remains. Even under these circumstances ten isomeric compounds of this composition may exist, although only two isomerides are known, viz. acetic acid and methyl formate. The properties and the character of acetic acid must be carefully studied and examined in order to ascertain which of the ten possible constitutional formulæ corresponds to the structure of this substance. And the manner in which the atomic chain can be split up and how built together again must also be ascertained.

Acetic acid, $C_2H_4O_2$, is formed from alcohol, $CH_3—CH_2—O—H$, by the replacement of O for H_2. Which are the two hydrogen atoms replaced by the atom of oxygen? The H contained in the hydroxyl is not one of the replaced atoms, for one of the hydrogen atoms in acetic acid differs essentially from the others in its properties. It is very easily replaced by metals and almost as easily by hydrocarbon radicals. These and similar observations show beyond doubt that in acetic acid one atom of hydrogen is united to oxygen and the three others to carbon. Hence it follows that one atom of oxygen is contained in the group hydroxyl, —O—H, as in the case of alcohol. In fact, one atom of oxygen and that atom of hydrogen which possesses properties differing from the rest can be easily displaced in the molecules of alcohol and of acetic acid; *e.g.*

$$\begin{array}{lrcl} \text{Alcohol} & C_2H_6O + PCl_5 & = & C_2H_5Cl + POCl_3 + HCl. \\ \text{Acetic acid} & C_2H_4O_2 + PCl_5 & = & C_2H_3OCl + POCl_3 + HCl. \end{array}$$

These and similar analogies induced Gerhardt to use the analogous formulæ for these two substances

$$\left.\begin{matrix} C_2H_5 \\ H \end{matrix}\right\} O \qquad\qquad \left.\begin{matrix} C_2H_3O \\ H \end{matrix}\right\} O$$

Alcohol. Acetic acid.

in which the radicals, ethyl C_2H_5 and acetyl C_2H_3O, correspond with each other. Only one arrangement of the atoms is possible in the case of ethyl. In acetic acid 'methyl' has long been regarded as a constituent or 'copula,' united with oxalic acid according to Berzelius,[1] with carbon according to Kolbe,[2] and with carbon monoxide according to Gerhardt.[3] The atomic linking of acetyl has been successfully established by Kekulé,[4] who has done much good service to the science in this class of investigation. The chief features of the ideas which guided him in his research are briefly described in the following.

The chain of atoms is broken by the dry distillation of an acetate with an alkaline hydrate; one atom of carbon escapes in combination with hydrogen as marsh gas, and the second carbon atom remains united to all the oxygen and metal in the compound, and also combines with the oxygen and metal of the alkali. It is therefore probable that one carbon atom is closely united with the metal and oxygen, and the other carbon atom is attached to the hydrogen of the acetate. Hence acetic acid has the formula $H_3C—CO—O—H$, which is completely confirmed by the whole character of the substance; *e.g.* by the following decompositions:

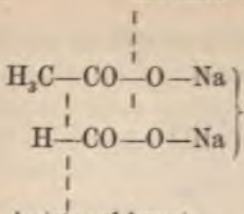
$$\left.\begin{matrix} H_3C—CO—O—Na \\ H—O—Na \end{matrix}\right\} = H_4C + NaO—CO—ONa.$$

Acetate and hydrate. = Marsh gas and carbonate.

[1] *Lehrbuch*, 5. deutsche Auflage, p. 709; *Jahresbericht*, 1844, pp. 95, 431.

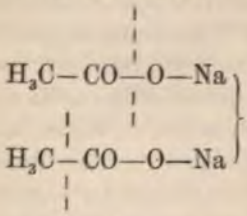
[2] *Handwörterbuch der rein. und angew. Chemie*, vi. 807; *Ann. Chem. Pharm.* 1860, cxiii. 297.

[3] *Traité de Chim. Org.* iv. 672. [4] *Lehrb. org. Chemie*, i. 521.



$$H_3C—CO—O—Na + H—CO—O—Na = H_3C—CO—H + NaO—CO—ONa.$$

Acetate and formate. = Aldehyde and carbonate.



$$H_3C—CO—O—Na + H_3C—CO—O—Na = H_3C—CO—CH_3 + NaO—CO—ONa.$$

Acetate and acetate. = Acetone. Carbonate.

Not only the chemical, but also the physical properties of acetic acid and its salts testify so strongly in favour of this arrangement of the atoms, that no other hypothesis appears trustworthy.

Similar arguments show that methyl formate, which is isomeric with acetic acid, has the constitution expressed by the formula $H_3C—O—CO—H$.

In addition to these two compounds only a third isomeride, containing the group CO, is possible, viz. the aldehyde of glycolic acid, $H—O—CH_2—CO—H$, which is not yet known, but will in all probability be discovered in the future.

Four ring-shaped arrangements of the atoms may also be imagined, and also three combinations in which the double linking of two carbon atoms $=C=C=$ occurs.

But whether all these imaginable combinations really correspond to possible positions of equilibrium of the atoms has not been decided.

§ 126. The somewhat difficult problem of ascertaining the arrangement of the atoms in a body of comparatively simple constitution, such as acetic acid, becomes much more complicated with an increased number of carbon atoms. In many cases, however, the investigation is much simplified by the chain of atoms splitting up into certain large groups of atoms the constitution of which is known or can be ascertained with a great degree of probability, or further by the possibility of

building up these compounds from such groups. Most striking examples of this description are to be found amongst the group of so-called aromatic compounds, all of which contain at least six, and frequently a larger number, of carbon atoms in the molecule: despite this it has in recent years been possible to investigate and study even the minutest details of their constitution. The rich and manifold results accruing from these investigations testify sufficiently to the utility of the theory of atomic linking and to its fertility in promoting the advancement of the science. The classic researches of Liebig and Wöhler on benzoyl compounds,[1] and of Mitscherlich on benzene,[2] at one time regarded as complete, have by its aid undergone great and remarkable extensions.

The theory by which it is sought to explain the arrangement of the atoms in the aromatic compounds is based on a fact first observed by Mitscherlich in the case of benzoic acid, viz. that all these compounds yield, on decomposition, a group of six carbon atoms (generally combined with not more than six hydrogen atoms), which are more firmly united with each other than with the other carbon atoms contained in the compounds, since these six atoms cannot be separated from each other by influences which induce the separation of the other carbon atoms from them.

Thus calcium carbonate and benzene, C_6H_6, are not only formed by the distillation of benzoic acid, $C_7H_6O_2$, and slaked lime, but the same products are obtained from mellitic acid, only in somewhat different proportions:

$C_7H_6O_2$	+	CaO_2H_2	=	C_6H_6	+	$CaCO_3$	+	H_2O.
Benzoic acid.		Calcium hydrate.		Benzene.		Carbonate.		Water.
$C_{12}H_6O_{12}$	+	$6CaO_2H_2$	=	C_6H_6	+	$6CaCO_3$	+	$6H_2O$.
Mellitic acid.		Calcium hydrate.		Benzene.		Carbonate.		Water.

Many acids and other compounds of the group of aromatic substances behave in a similar way. Many of these bodies can be artificially prepared by joining together the separate atomic chains.

On account of these and many similar facts, benzene has long been regarded as a radical occurring in aromatic compounds.

§ 127. The theory of atomic linking gave rise to the

[1] *Ann. Pharm.* iii. 249, 1832. [2] *Pogg. Ann.* xxix. 231, 1833.

problem of satisfactorily explaining the firm union of these six carbon atoms and the other special properties of this group. Kekulé [1] has solved this problem by a happily chosen hypothesis, which has so far been confirmed by the behaviour of these bodies, and which agrees essentially with observed facts, even if the hypothesis requires a slight modification, as is the opinion of some chemists.

The extraordinary number of possible isomeric compounds containing six carbon atoms and six monovalent atoms makes it appear at first sight hardly possible to discover the constitution of such a group. But the careful study of benzene and its derivatives has limited the number of really possible atomic arrangements to such an extent as to restrict the choice to a small number only.

A large number of new compounds are formed from benzene by substituting chlorine, bromine, iodine, and other atoms, or chains of atoms, for hydrogen. No cases of isomerism have been observed in any of the substitution products in which only one atom of hydrogen in the benzene has been so replaced, although isomerism regularly occurs in most other hydrocarbons, even in those which only contain three carbon atoms (see § 116). But isomerism is observed as soon as a second hydrogen atom is replaced by an atom of a different description; more than three isomeric substitution products of this kind have never been observed, even when the two hydrogen atoms are replaced by two dissimilar atoms or atomic chains. But when three hydrogen atoms are replaced the number of isomerides is increased by the substitution of dissimilar elements; but our present knowledge does not yet suffice to enable us to decide with certainty the maximum number of these isomerides.

Assuming that these results of observation are perfectly correct, we are led to the following conclusions:

(1) The six hydrogen atoms contained in benzene, and consequently the carbon atoms to which they are attached, are all united in the same way, so that it is quite immaterial which of the hydrogen atoms is replaced.

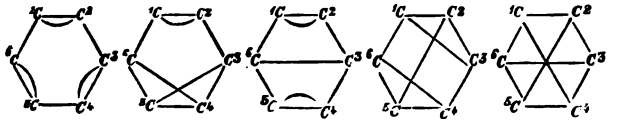
[1] *Bull. Soc. Chim.* 1865, 98; *Zeitschr. f. Chemie*, 1865, 176; Kekulé, *Lehrbuch org. Chem.* ii. 493; *Ann. Chem. Pharm.* 1872, clxii. 77.

(2) With reference to one of the hydrogen atoms, the five others may occupy three different positions; therefore some of these occupy the same relative position to the first atom.

The only hypothesis capable of explaining these results is that the six atoms of hydrogen are equally distributed among the six carbon atoms, and that the six pairs of atoms, CH, form a continuous circular chain. But as each carbon atom has three affinities available for union with the others, the chain need not of necessity form a single ring, but may be a complicated, netlike structure. It is only necessary that all the carbon atoms should be linked together in exactly the same fashion. If the existence of free affinities is assumed, then this condition is only fulfilled by the hypothesis of a simple ring of six members; but in the case of double linking of the carbon atoms by the available affinities only two of the five possible ring-shaped arrangements of the atoms satisfy this condition. Let C^1, C^2, C^3, C^4, &c., indicate the six carbon atoms, and let the corresponding indices at the foot of each C denote the carbon atoms with which it is directly united, then the five following combinations are obtained:

I.	II.	III.	IV.	V.
C^1_{622} C^2_{131}	C^1_{622} C^2_{131}	C^1_{622} C^2_{131}	C^1_{623} C^2_{135}	C^1_{624} C^2_{135}
C^3_{244} C^4_{353}	C^3_{245} C^4_{356}	C^3_{246} C^4_{355}	C^3_{241} C^4_{356}	C^3_{246} C^4_{351}
C^5_{466} C^6_{515}	C^5_{463} C^6_{514}	C^5_{464} C^6_{513}	C^5_{462} C^6_{514}	C^5_{462} C^6_{513}

or, represented graphically:

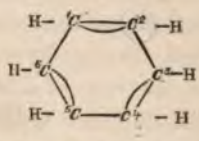


These formulæ are not intended to indicate that the atoms are arranged in a circle in space, but only to show which atoms are in direct union with each other. For instance, the relative position of the atoms in space may be the same as the angles of a regular octahedron, the affinities uniting the atoms would then act in the direction of nine of the twelve edges of the octahedron. Of the five possible combinations only the

first and the two last satisfy the condition of all the carbon atoms, being linked together in precisely the same fashion. Kekulé prefers the first formula, since at present it appears to offer a better explanation of the isomerism of the substitution products than the other formulæ. There is a close resemblance between Kekulé's formula and the conception of a ring-formed chain, each carbon atom having a free affinity. The constitution of benzene is represented by these two formulæ thus:

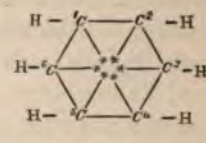
Kekulé's formula.

I.



Free affinities.

VI.



The existence of not more than three isomeric products when two atoms of hydrogen are replaced by two dissimilar atoms is explained by either of these formulæ, but the second formula affords the simplest explanation. If the H at C^1 is replaced, then the second substitution may take place at any of the remaining five carbon atoms. But two of these, viz. C^2 and C^6, are in direct combination with C^1. An atom uniting with either of these will occupy the same relative position with reference to the atom combined with C^1; consequently these two substitution products are identical. The same is true of the atoms combined with C^3 and C^5, whilst the atom attached to C^4 has a peculiar position. In accordance with observation, three different substitution products are possible in which the hydrogen atoms are replaced at

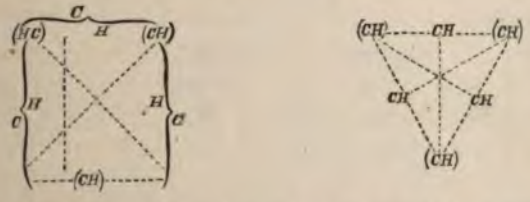
(1) C^1 and C^2 or C^6
(2) C^1 ,, C^3 ,, C^5
(3) C^1 ,, C^4

This is not quite true of Kekulé's formula in its original form, since no difference is made between the single and double linking of the carbon atoms. If this difference is taken into account, C^2 and C^6 occupy different positions with regard to C^1, and the same is also true of the hydrogen atoms attached to these carbon atoms. Four, or even five, disubstitution

products would thus be possible, which is in contradiction to our present experience. In order to avoid this difficulty Kekulé[1] brought forward a hypothesis which virtually amounts to the assumption that each carbon atom oscillates in such a way that it is alternately in union or contact with each of its neighbours.

The formula with six free affinities satisfactorily explains these facts, and also accounts for the fact that benzene readily unites with six chlorine or bromine atoms forming benzene hexachloride, $C_6H_6Cl_6$, or benzene hexabromide, $C_6H_6Br_6$. But, as far as we can judge at present, Kekulé's formula is more perfectly in unison with the optical properties described in § 142, and formulæ IV. and V. agree better with the thermic properties of the benzene compounds.

Formula V. exhibits a certain amount of analogy to Kolbe's[2] formula for benzene, $\left.\begin{matrix}CH\\CH\\CH\\H_3\end{matrix}\right\} C_3$, according to which benzene is composed of three molecules of methane, in which the hydrogen atoms are replaced by three groups of the trivalent radical methine CH, so that each methine replaces an atom of hydrogen in each methane, and is consequently subordinated to it. Formula V. is easily derived from this treble marsh gas type, thus;



And it is easy to represent three of the six CH groups which form the ring, viz. the three denoted thus (CH), as subordinated to the other three (compare § 117).

The same formula is arrived at by attaching a different value to the even and uneven carbon atoms in V.

[1] *Ann. Chem. Pharm.* 1872, clxii. 86.

[2] Introduction to the section 'Aromatische Verbindungen.' See note, p. 221.

isomeric monochlorobenzoic acids. Theory predicts the existence of the following compounds:

$HO—CO—CH_3$		$HO—CO—CH_2Cl$
Acetic acid	yields	monochloracetic acid
$HO—CO—C_6H_5$		$HO—CO—C_6H_4Cl$
Benzoic acid	yields	three isomeric monochlorobenzoic acids,

which are distinguished from each other by the chlorine atom occupying the three different positions described in § 127.

In fact, three isomeric compounds are known which differ in their properties and are distinguished by the names ortho-, para-, and meta-chlorobenzoic acids. By replacing the chlorine or carboxyl group by another atom or group of atoms three isomeric compounds can again be obtained. Similar behaviour is exhibited by the other aromatic compounds, which may be regarded as disubstitution products of benzene, having the formula C_6H_4XY, where X and Y represent monovalent atoms or radicals. Three isomeric modifications of such compounds are possible, and are, indeed, generally known.

The determination of the relative position which the different atoms and radicals occupy in the molecule of these compounds is at present one of the most important problems in organic chemistry, and one which receives a large share of attention and labour. But the methods used in solving this problem were formerly so uncertain and untrustworthy that it is by no means a rare occurrence for views which have at one time been universally accepted as correct to be overthrown and to be replaced by directly opposite ideas.

Hydroquinol, one of the three isomeric dihydroxybenzenes, $C_6H_4(OH)_2$, may be taken as an example from numerous similar cases. Within a space of not quite two years each of the three possible arrangements of the atoms (1 : 2, 1 : 3, and 1 : 4) has been successively assigned to it.[1]

§ 129. Convinced of the very great difficulty of determining the absolute position of the atoms, we are often contented with a relative determination of their position, and attempt to ascer-

[1] See Fittig, *Grundriss der organ. Chemie*, Ausgabe von 1874, 338 and 627.

tain in which compounds the atoms or radicals substituted for hydrogen occupy one and the same relative position. As a rule, we start with the assumption that this is the case in those compounds which can be obtained from each other by substitution. In many cases, however, this assumption is clearly incorrect. The new atom or radical does not always occupy the position of the atom it displaces. On the contrary, it not unfrequently happens that other atoms or groups of atoms exchange or otherwise alter their places during the reaction.

An atomic group can thrust itself into the molecule and change the original sequence of the atoms. For example, Berthelot discovered that carbon monoxide unites with potassium hydroxide to form a formate. It cannot be assumed that potassium hydroxide is contained in the formate as a united group of atoms, since such a group does not fulfil the conditions [1] necessary to the existence of the molecule.

We must therefore assume that the carbon monoxide thrust itself between the hydrogen and the group KO: $*—CO* + K—O—H = K—O—CO—H$.

The formation of sodium propionate, $NaO—CO—C_2H_5$, from carbonic anhydride, CO_2, and sodium ethide, NaC_2H_5, which was first discovered by Wanklyn,[2] is an analogous case. A much more frequent occurrence is that the exchange of one or more atoms or radicals in the molecule produces a state of unstable equilibrium in the atomic chain, consequently during or immediately after the exchange, the atoms assume a position of stable equilibrium, and the substance first formed is converted into a metameric compound.

The artificial formation of urea, discovered by Wöhler in 1828, is a classic example of this nature. Cyanic acid, $N\equiv C—O—H$, or isocyanic acid, probably $O=C=N—H$ and ammonia NH_3, unite to form ammonium cyanate, which in the course of time changes into urea. The arrangement of the atoms in urea must be $H_2=N—CO—N=H_2$, since it is formed by substituting NH_2 for Cl in $Cl—CO—Cl$.

Ethylene chloride and ethylidene chloride, $ClH_2C—CH_2Cl$,

[1] *Vide* § 106.

[2] The fact that the molecular weight of some of these substances has not been directly determined is immaterial.

and $H_3C—CHCl_2$, are also examples of the same fact. As a rule, different products are formed when the chlorine atoms in these compounds are replaced by other atoms or radicals. The products are not identical, but only isomeric, because the new atoms or groups of atoms fill the position occupied by chlorine atoms. But under certain conditions, especially when the reactions take place at high temperatures, the products from both bodies are identical, because an intermolecular change has taken place in one of the two substances.

The aromatic compounds offer numerous examples of this kind. The most remarkable are (1) the transference of methyl from the nitrogen of aniline into the benzene nucleus, observed by A. W. Hofmann.[1]

$$C_6H_5—N(CH_3)_3I = CH_3—C_6H_4—N(CH_3)_2HI$$
$$= (CH_3)_2—C_6H_3—N(CH_3)H_2I = (CH_3)_3—C_6H_2—NH_3I,$$

and (2) the transformation of the three isomeric oxybenzoic acids into each other, discovered by Kolbe and his pupils.[2] Since this kind of change takes place more frequently at high temperatures, conclusions as to the arrangement of the atoms which are based on the exchange of certain atoms or radicals are rightly regarded as uncertain, when these changes can only be brought about at high temperatures.

§ 130. The consideration of the few comparatively simple examples described in the preceding paragraphs is sufficient to indicate how difficult, but also how remunerative, is the investigation of atomic linking in different compounds. It is not surprising that in the case of a large number of organic compounds the difficulties of the investigation have not yet been overcome.

For very complex compounds, or for compounds which have not been thoroughly investigated, the number of decompositions known is not sufficient to enable us to state which of the atoms are directly united with any one given atom. Certain groups of atoms are, therefore, of necessity left unresolved, as compound radicals in the structural formulæ of such compounds. This is also frequently done for the sake of

[1] *Ber. d. deut. chem. Ges.* 1872; 704 and 720.

[2] *Journ. f. pr. Chem.* 1874, x. 451; 1875, xi. 24 and 385; 1876, xiii. 103.

convenience in the formulæ of those compounds whose members could be represented in full.

For many years the formula of benzoic acid could only be separated into the groups (C_6H_5)—CO—OH. The radical 'phenyl,' C_6H_5, had to remain unresolved. This same formula is still frequently used, since in many of the decompositions of benzoic acid this radical remains unchanged. But as in many important reactions the group C_7H_5O, or C_6H_5—CO, the radical 'benzoyl' remains unaltered, this radical is also frequently left in the formula, and Gerhardt's formula used, $\left.\begin{matrix}C_7H_5O\\H\end{matrix}\right\}O$ or C_7H_5O-OH. Similarly Gerhardt's formula $\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O$ or C_2H_3O—OH is frequently used instead of the structural formula for acetic acid, because the radical 'acetyl' remains unchanged in many reactions.

In the present state of our knowledge the extent to which a formula is split up or contracted is a mere matter of convenience, and has ceased to be a subject of scientific discussion, as was formerly the case. It is only necessary that the groups which are left as radicals should comply with the conditions as to their structure previously mentioned (§ 106), and that they in reality remain together in certain decompositions.

But it is no longer permissible to accept groups of atoms which do not comply with these conditions as constituents of volatile compounds.

§ 131. Our knowledge of atomic linking would undoubtedly remain in a state of uncertainty if it was entirely and solely based on the investigation of the decomposition and rebuilding of the atomic chains. Fortunately new auxiliary methods were discovered at the very commencement of this research, which added largely to the accuracy and extent of our knowledge. Long before the theory of atomic linking was developed, identity or similarity in the chemical character and physical properties of bodies was believed to indicate, as a rule, identity or similarity of constitution.

This idea has been more closely examined, and to a certain extent confirmed, by researches on atomic linking.

As soon as the constitution of a large number of compounds

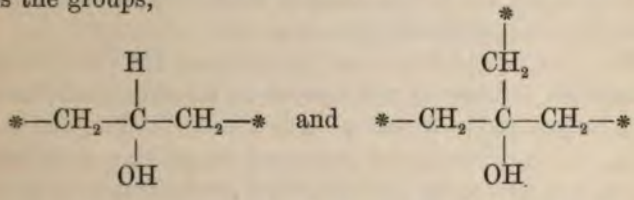
had been accurately determined, it was seen that substances having analogous properties must, as a rule, possess an analogous arrangement of the atoms. At the same time it was evident that certain groups of atoms exert a much stronger influence on the nature of the compound than others, so that the character of a compound is often determined by a small number of the atoms it contains, if these are united together in a particular manner.

Analytical chemistry long ago discovered the connection between the properties of a body and those of its constituents. Systematic chemistry, but especially organic chemistry, is now investigating the influence which certain groups of atoms exert on the chemical and physical properties of compounds. The most important results of this investigation are now described in many textbooks. A thorough and systematic account of these results would form an extensive and highly desirable treatise, but space only permits us to offer a few examples.

§ 132. The chemical behaviour of the elements, their tendency to form compounds with other elements, depends not only on their own nature, but to a great extent on the nature of the compounds in which they are contained. It has long been known that one and the same element can unite with different elements and form compounds of widely distinct properties, and that in these different compounds the element is held in position by unequal forces. The compounds of hydrogen with carbon, nitrogen, oxygen, and chlorine exhibit widely different properties, and the hydrogen is much more readily replaced by other elements in some of these compounds than in others. The hydrogen atoms contained in one and the same molecule may also exhibit a similar difference, according as they are directly united to carbon, nitrogen, oxygen, or sulphur. Thus an atom of hydrogen which is directly attached to carbon is more easily replaced by negative elements like chlorine or bromine, and a hydrogen atom directly combined with oxygen is more easily replaced by positive elements, and especially by metals.

The more distant atoms also often exert considerable influence. The properties of the hydrogen atoms of the hydroxyl group, —OH, vary with the nature of the atom which saturates

the second affinity of the oxygen atom. Potassium forms with hydroxyl the powerful base potash, KOH; hydrogen forms water, HOH; and chlorine yields hypochlorous acid, ClOH. The influence of the neighbouring atoms is even greater. The character of a hydroxyl group attached to a carbon atom varies according as the remaining affinities are saturated by positive or negative elements. The groups of atoms $\times$—CH_2—OH and $\times$—CO—OH are characteristic of large groups of organic compounds, the first is characteristic of the so-called primary alcohols, and the second, known as the 'carboxyl' group, of the organic acids. Still finer distinctions can be drawn. Thus the groups,



are recognised as typical of the secondary and tertiary alcohols, and the hydroxyl group attached to the benzene ring (§§ 127, 128) differs from all the others in its properties. It holds a position between the alcoholic and acid hydroxyls; when an atom of hydrogen in the benzene ring is replaced by a negative atom or radical, its behaviour approaches that of an acid.

Phenol, C_6H_5—OH, is a very weak acid. Trichloro- and trinitro-phenols, $C_6H_2Cl_3$—OH and $C_6H_2(NO_2)_3$—OH, are powerful acids, behaving like those acids in which —OH is attached to —CO—.

Other groups of atoms and individual atoms exhibit similar differences to those observed in the case of hydroxyl, according to the nature and arrangement of the atoms with which they are directly or indirectly united.

But as the subject is usually exhaustively dealt with in modern treatises on organic chemistry it is not necessary to discuss it in detail in the present work.

§ 133. The arrangement as well as the nature of the atoms in a compound exerts a definite influence on the physical properties of the substance. The knowledge of the connection is of great service in investigating atomic linking. When

the nature of the connection between the physical properties and chemical constitution is ascertained in a series of compounds of known structure, the law governing this relation can be used in order to deduce from the physical properties of a compound the arrangement of its atoms, in cases where this is not known. The properties are not very numerous for which this relation with the atomic linking has been determined with sufficient exactitude for a large number of compounds. In many of the carbon compounds the influence of the arrangement of the atoms on their *volatility* can be expressed by simple rules, which are indeed neither very general nor very exact, but within certain limits represent the law of this connection at least approximately.

The fact that the law of the relation between volatility and atomic linking is not known in its strict form, in spite of the large number of compounds investigated, is due to two causes, viz. the difficulty of preparing the substances in a state of purity, and secondly the method of representing the relation between atomic linking and volatility, which is convenient in practice, but ill-adapted for theoretical considerations.

The measure of the volatility of a substance is its vapour pressure, *i.e.* the maximum pressure which the vapour can support without being condensed to a liquid. This maximum pressure is dependent on the temperature; it increases with the temperature, but not in the same ratio. For a given substance a certain vapour pressure corresponds to each temperature, so that each of these variable values appears to be governed by the other. But it is obvious that the temperature must be regarded as the independent variable and the vapour pressure as the dependent variable; for the pressure of a gas or vapour is produced by the motion of its particles, which is imparted to it in the form of heat and is measured by the temperature, the degree of heat. This relation has been reversed in the investigation of the connection between volatility and chemical constitution. Instead of investigating the changes in the vapour pressure of different compounds

[1] See Kopp, *Ann. Chem. Pharm.* 1855, xcvi. 2; *Lehrbuch phys. theor. Chemie*, 1863, 202; Kekulé, *Lehrbuch org. Chem.* i. 281; Gmelin, *Kraut*, i. 1; Alex. Naumann, 552.

with the temperature, the vapour pressure has, as a rule, been treated as the independent variable, and the temperature has been determined at which all the different bodies possess the same vapour pressure, viz. that equal to the atmospheric pressure. In other words, the boiling points have generally been determined only at the atmospheric pressure. The problem has been solved in its entirety only in the case of a few groups of compounds.[1]

Although the observations are incomplete in the case of most substances, they may serve nevertheless in many cases, especially for the carbon compounds as a valuable aid in the investigation of atomic linking.

This application has been rendered possible by the discovery that the boiling point is dependent to a definite extent on the molecular weight and on the arrangement of the atoms. The following rules, the results of observation, are particularly serviceable.

§ 134. Isomeric substances of the same molecular weight and analogous atomic linking possess almost the same boiling points. H. Schröder [2] pointed out (on insufficient grounds) that the boiling points are not exactly the same. Linneman,[3] who used an improved process of distillation, confirmed the accuracy of this statement with regard to a large number of groups. The isomeric ethereal salts of acids of analogous constitution have almost the same boiling point.

	B. Pt.[4]
Butyl acetate, $CH_3—CH_2—CH_2—CH_2—O—CO—CH_3$ . .	124·3
Propyl propionate, $CH_3—CH_2—CH_2—O—CO—CH_2—CH_3$.	122·4
Ethyl butyrate, $CH_3—CH_2—O—CO—CH_2—CH_2—CH_3$ . .	121·0

The boiling point rises as the chain attached to the CO decreases and the chain attached to the O increases in length.[5]

[1] Landolt's determinations of the vapour tensions of the fatty acids, *Untersuchungen über die Dampftensionen homologer Verbindungen*, Bonn, 1868; also *Ann. Chem. Pharm.* 1868, Suppl.-Band vi. 129; Winkelmann, *Ann. Chem. Pharm.* 1880, cciv. 251. See also Schumann's investigations of the ethereal salts of these acids, *Wied. Ann.* 1881, xii. 40.

[2] *Die Siedhitze der chem. Verbindungen*, Mannheim, 1844, § 57.

[3] Ed. Linnemann, 'Ueber Siedepunktsdifferenzen,' *Ann. Chem. Pharm.* 1872, clxii. 39.

[4] Linnemann, *loc. cit.*

[5] Schumann (*loc. cit.*) has shown that this rule does not apply to methyl ethereal salts, which boil at higher temperatures than their isomeric ethyl salts.

Isomeric compounds of the same molecular weight, but not having analogous atomic linking, generally possess different boiling points; a certain difference in atomic linking generally corresponds to a definite difference between the boiling points. The ethereal salts of the composition $C_nH_{2n}O_2$ differ from the isomeric acids by containing the group $-OC_mH_{2m+1}$ in the place of hydroxyl. This causes a difference of about 85° in the boiling points.

	B. Pt.
Propionic acid, HO—CO—CH_2—CH_3	140°
Methyl acetate, CH_3—O—CO—CH_3	56°
Diff.	84°
Ethyl formate, CH_3—CH_2—O—CO—H	55°
Diff.	85°
Butyric acid, HO—CO—CH_2—CH_2—CH_3	162°
Ethyl acetate, CH_3—CH_2—O—CO—CH_3	77°
Diff.	85°

The boiling points differ generally in compounds having analogous atomic linking but different molecular weights; a given difference in composition generally corresponds to a definite difference in the boiling points.

In many series of homologous compounds the boiling point is raised 19 or 20 degrees for each additional carbyl group, CH_2; *e.g.* the fatty acids.[1]

	B. Pt.	Diff.
Formic acid, HO—CO—H	100°	
Acetic acid, HO—CO—CH_3	119°	19°
Propionic acid, HO—CO—CH_2—CH_3	140°	21°
Butyric acid, HO—CO—CH_2—CH_2—CH_3	162°	22°

Landolt has determined the vapour pressure as a function of the temperature for these and some other bodies, and has shown that almost the same differences between the boiling points exist for increased as well as for diminished pressures, viz. for all pressures between one and a half and half an atmosphere. But when the pressure sinks below half an atmosphere the differences between the boiling points are no longer equal.

In other series of organic compounds of analogous atomic linking, a difference in the composition of CH_2 also produces

[1] Landolt, *op. cit.* p. 40.

a constant rise in the boiling point, which is in some cases much greater, in others much smaller than 20°.

The boiling points of the ethereal salts of the hydroxy-acids, such as glycollic acid, which were investigated by L. Schreiner,[1] are very remarkable:

$$C_mH_{2m+1}—O—CH_2—CO—O—C_nH_{2n+1}.$$

The accompanying table shows that the increase of m by one unit raises the boiling point twenty degrees and more, whilst a similar addition to n only produces an alteration of 6° or 8°.

	$m = 0$	Diff.	$= 1$	Diff.	$= 2$	Diff.	$= 3$
$n = 0$	—		158°	21°	199°		?
Diff.			—45		—47		
$n = 1$	151	—18°	133	19	152	26	178
Diff.	9		6		6		6
$n = 2$	160	—21	139	19	158	26	184
Diff.	10		8		8		8
$n = 3$	170	—23	147	19	166	26	192

A certain difference in composition and atomic linking generally produces the same difference in the boiling point, even in the case of bodies differing in composition and atomic linking. The addition of CH_2 lowers the boiling point about 62°, when it is produced by the substitution of methyl CH_3 for the H of a hydroxyl group, so that the O no longer links H and C together, but unites C with C; *e.g.*[2]

	B. Pt.
Acetic acid, H—O—CO—CH_3	119°
Methyl acetate, CH_3—O—CO—CH_3	56°
Diff.	63°
Alcohol, H—O—CH_2—CH_3	78°
Ethylmethyl ether, CH_3—O—CH_2—CH_3	11°
Diff.	67°

In the compounds investigated by Schreiner a similar change of composition only lowers the boiling-point 45–47°, or even

[1] Inaugural Dissertation, Tübingen, 1878; *Ann. Chem. Pharm.* 1879, cxcvii. 1. On pp. 8 and 20 the boiling point of the methyl ether of ethylglycollic acid is incorrectly given as 142° instead of 152°.

[2] The difference is smaller when the hydroxyl is combined with phenyl, as shown by comparing the boiling points of anisol and phenol, viz. 182° and 152°.

only 18–23°, according to the particular hydroxyl group which is converted into O—CH_3.

If an alcohol group,[1] CH_2—OH, is converted into carboxyl CO—OH, by oxidation, the boiling point is, as a rule, raised about 40°.

	B. Pt.
Methyl alcohol, HO—CH_3	60°
Formic acid, HO—CO—H	100°
Diff.	40°
Ethyl alcohol, HO—CH_2—CH_3	78°
Acetic acid, HO—CO—CH_3	119°
Diff.	41°
Benzyl alcohol, HO—CH_2—C_6H_5	207°
Benzoic acid, HO—CO—C_6H_5	250°
Diff.	43°

Large numbers of similar relations have been discovered, but in many cases they have not been ascertained with sufficient certainty, especially where there is more than one point of difference in composition and atomic linking.

§ 135. If the law governing the relation between volatility and atomic linking was perfectly understood, it is highly probable that the knowledge of the percentage composition and of the vapour pressure as a function of the temperature would be sufficient in any case to definitely determine the atomic linking, and thus to select from the numerous possible forms of combination that one which belongs to the given compound. This is by no means usual in the present state of our knowledge; in certain cases only (which are, however, pretty numerous) it is possible to do so by applying the empirical rules on the relation between volatility and atomic linking contained in the preceding paragraphs. In order to apply these laws it is generally necessary to know the atomic linking and volatility of a large number of compounds resembling in composition or properties the substance whose atomic linking it is wished to ascertain. Thus the boiling point would easily solve the problem in § 124, viz. which of the two possible atomic combinations for the compound C_2H_6O is to be assigned to alcohol and which to methyl ether. Experience shows that

[1] See § 132.

the hydroxyl compound is always less volatile and has a higher boiling point than its isomeric compounds which do not contain hydroxyl, hence the constitution $CH_3—CH_2—OH$ is assigned to alcohol, which boils at 78°, and $CH_3—O—CH_3$ to methyl ether, which boils at −21°. In this and many other cases the result is merely an almost superfluous confirmation of the knowledge acquired by splitting up and building together again the atomic chains. The question whether a compound $C_nH_{2n}O_2$ contains the carboxyl group, and is an acid, or whether its atoms are arranged as an ethereal salt would scarcely be decided by the fact of the acid boiling 85° higher than the isomeric ethereal salt, for whether the compound exhibited the properties of an acid or an ethereal salt would be first ascertained. Where a doubt existed with regard to these properties, and when the splitting up and building together of the chain did not yield decisive results, then the determination of the volatility may be of service. But it cannot be disputed that less importance is attached to this auxiliary than it deserves; for it is free from the source of error mentioned in § 129, which often makes the deductions from chemical reactions very uncertain. It has been already pointed out that the study of chemical changes alone does not insure the attainment of a perfectly reliable conclusion as to the atomic linking *before* the reaction, since a greater change in the constitution of the body may occur than is absolutely required by the reaction. In investigating the chemical behaviour of a substance, we ascertain the arrangement of the atoms at the moment when its equilibrium is disturbed, but in determining the physical properties, this is ascertained during the state of equilibrium.

On the other hand, it cannot be denied that a direct conclusion as to the arrangement of the atoms is deduced from the chemical reactions, whilst deductions from the physical properties are indirect, and can only be made after the atomic linking of a large number of compounds has been ascertained by chemical means, and after the connection between the physical properties and the atomic linking has been subsequently determined. It is therefore obvious that the know-

ledge of this connection must long be a secondary consideration, although it will gradually increase in importance.

At present the determination of the boiling point is useful for ascertaining the atomic linking of those isomeric bodies which resemble each other so closely that they can only be distinguished with difficulty, or whose constitution requires further confirmation.

These fine distinctions are exhibited by those isomeric compounds mentioned in § 117, which differ from each other in the linking of their carbon atoms, or in the different positions occupied by other atoms. The analyses and syntheses of these compounds and the comparison of their physical properties show that the isomeric compounds, whose atoms form a straight chain, have the highest boiling points, and that the boiling point sinks as the chief chain diminishes in length and the number of side chains increases.

The four different butyl alcohols, $C_4H_{10}O$, whose atomic linking is represented below, have the following boiling points:

	B. Pt.
Normal butyl alcohol, $CH_3—CH_2—CH_2—CH_2—OH$	117°
Isobutyl alcohol, $CH_3—CH(CH_3)—CH_2—OH$	109°
Secondary butyl alcohol, $CH_3—CH_2—CH(OH)—CH_3$	97°
Tertiary butyl alcohol, $CH_3—C(CH_3)(OH)—CH_3$	84°

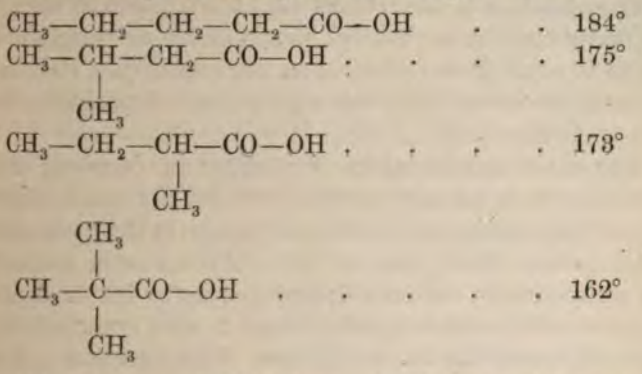
The first two alcohols on oxidation yield two different butyric acids, having the constitutional formulæ

$$CH_3—CH_2—CH_2—CO—OH \quad \text{and} \quad CH_3—CH(CH_3)—CO—OH$$

The acid formed from the second alcohol, and therefore called isobutyric acid, having the constitution represented by the second formula, boils at 154°, normal butyric acid derived from the first alcohol boils at 162°.

Similarly the four different valerianic acids, $C_5H_{10}O_2$, boil

at 162°, 173°, 175°, and 184° respectively. The linking of their atoms is represented by the following formulæ:



Since the difference of 22° between the boiling point of one of these valerianic acids (b. p. 184°) and the boiling point of normal butyric acid (160°) is the same as the difference between the boiling point of the latter acid and that of propionic acid (140°), we should be justified in assuming the acid boiling at 184° to be normal valerianic acid, even if its mode of formation had not led to the same conclusion. The boiling point of the second valerianic acid differs from that of isobutyric acid by almost the same interval, viz. 21°; the second formula, which is analogous to that of isobutyric acid, is therefore assigned to it. The third formula is given to the acid boiling at 173°,[1] because it is derived from acetic acid by replacing one atom of hydrogen by CH_3 and another by C_2H_5; finally the acid boiling at 162° receives the last of the four possible formulæ, because it is derived from an alcohol having an analogous constitution. Relations similar to those which have been pointed out for the hydroxyl and carboxyl compounds have also been established for the corresponding chlorides, bromides, iodides, &c. At present it is impossible to formulate general laws for deducing the atomic linking from the observation of the boiling point. These examples suffice to show how the knowledge of the volatility can be successfully applied in determining atomic linking in certain rather small groups of compounds.

[1] R. Sauer, *Ber. d. deut. chem. Ges.* 1875, viii. 1037.

§ 136. Theoretical speculations on the influence of atomic linking on volatility may appear premature. We therefore confine ourselves to the remark that the position of the centre of gravity and the moment of inertia of the rotating molecule appear to exert great influence on the volatility. Determinations of the latent heat of vapours would probably throw light on this subject.

The easier condensation of compounds composed of long atomic chains is perhaps partly due to the elongated molecules mutually interfering with each other's path in their movements in the gaseous state, and to their colliding more frequently, and consequently condensing more easily to larger aggregations than the more compact molecules with branched chains would do under similar conditions. This question may perhaps be decided by observations on the rates of transpiration of the vapours.[1]

§ 137. There is no doubt that the fusibility of compounds depends on their atomic linking, so that it will be possible to make use of the melting point to discover the arrangement of the atoms.[2] But in the present state of the science this can only be done to a very limited extent. A rule which is frequently used in the case of isomeric substitution products of benzene (§ 127) is that *para* compounds melt at a higher temperature than the *ortho* and *meta* compounds.

The rise and fall of the melting point by repeated direct substitution of one and the same element in benzene is very remarkable. By the action of chlorine and bromine the following substitution products are successively obtained (together with small quantities of isomerides):

	Melting-point[3]			Melting-point
C_6H_6	+ 3°		C_6H_6	+ 3°
$C_6H_5Cl_1$		−40°	$C_6H_5Br_1$	below −20°
$C_6H_4Cl_2$	+ 53°		$C_6H_4Br_2$	+ 89°
$C_6H_3Cl_3$		+17°	$C_6H_3Br_3$	+44°
$C_6H_2Cl_4$	+139°		$C_6H_2Br_4$	+140°
$C_6H_1Cl_5$		+86°	$C_6H_1Br_5$	above 240°
C_6Cl_6	+228°		C_6Br_6	above 310°

[1] *Ann. Chem. Pharm.* 1863, Suppl. v. 129; *Ann. Phys. Chem.* 1879, vii. 497.

[2] Carnelly, *Phil. Mag.* [5] 1882, 13, 112, 180.

[3] Jungfleisch, *Compt. Rend.* 1867, lxvi. 911.

The substitution of the first, third, and fifth chlorine atom, and of the first and third bromine atom, lowers the temperature 40°, while the second, fourth, and sixth raise it again about 100°. The fifth bromine atom proves an exception; it also raises the melting point.

The relations which A. Baeyer[1] discovered between the melting points of the normal acids, $C_nH_{2n}O_2$, and $C_nH_{2n-2}O_4$, may be regarded from the same point of view. These acids have the composition

$$H—(CH_2)m—CO—OH \text{ and } HO—CO—(CH_2)m—CO—OH,$$

and may be regarded as derived from formic acid, H—CO—OH, and oxalic acid, HO—CO—CO—OH, by the introduction of $m(CH_2)$. Here again the melting point rises and falls with an increasing number of carbon atoms.

	Melting-point		Melting-point
$C_1H_2O_2$		+8·6°	
$C_2H_4O_2$	+17°		
$C_3H_6O_2$		below −21°	
$C_4H_8O_2$	+ 1°		
$C_5H_{10}O_2$		below −16°	
$C_6H_{12}O_2$	− 2°		
$C_7H_{14}O_2$		−10·5	
$C_8H_{16}O_2$	+16°		
$C_9H_{18}O_2$		+ 12°	
$C_{10}H_{20}O_2$	+30°		
—		—	
$C_{16}H_{32}O_2$	+62°		
$C_{17}H_{34}O_2$		+ 60°	
$C_{18}H_{36}O_2$	+69°		

	Melting-point	
$C_2H_2O_4$	does not melt	
$C_3H_4O_4$		+132°
$C_4H_6O_4$	+180°	
$C_5H_8O_4$		+ 97°
$C_6H_{10}O_4$	+148°	
$C_7H_{12}O_4$		+103°
$C_8H_{14}O_4$	+140°	
$C_9H_{16}O_4$		+106°
$C_{10}H_{18}O_4$	+127°	
$C_{11}H_{20}O_4$		+108°
—	—	
$C_{17}H_{32}O_4$		+132°

In passing from an uneven to the next even number of carbon atoms, the melting point rises; in passing from the even to the uneven numbers it falls. Taking each series of even and uneven members separately, the melting point first sinks in each series with an increased number of carbon atoms, and begins to rise again with the fifth and sixth members, except in the case of the even dibasic acid series, where it continues to sink to the tenth member and perhaps farther. Similar relations can be detected in many groups of organic compounds, but a general insight of the laws on which they are based is still wanting.

§ 138. The density of the compounds is another of the

[1] *Ber. d. deut. chem. Ges.* 1877, 1286.

properties which is influenced by the nature of their atomic linking. According to Kopp's[1] investigations the specific or molecular volumes, *i.e.* the space occupied by the molecular weights, of organic compounds in the liquid state, bear a simple regular relation to each other if the volumes are measured at temperatures at which the vapours of all the different liquids have the same vapour pressure. So far the comparison has only been made for temperatures at which this pressure is equal to that of one atmosphere, *i.e.* at the temperature of the boiling points under the mean atmospheric pressure. The weight of an atom of hydrogen is taken as the unit of weight, and the space occupied by the same weight of water at 4° as the unit of volume; then, according to Kopp's investigations,[2] the molecular volume, *i.e.* the volume occupied by the molecular weight of an organic compound of the composition $C_xH_yO_z$, or, in other words, the molecular weight $\mathfrak{M} = x \cdot 12 + y + z\,16$[3] divided by the density compared with water at 4°, is represented by the formula, which has been discovered empirically,

$$\frac{\mathfrak{M}}{d} = V = x \cdot 11 + y \cdot 5{\cdot}5 + z \cdot 7{\cdot}8;$$

or by

$$\frac{\mathfrak{M}}{d} = V = x \cdot 11 + y \cdot 5{\cdot}5 + z \cdot 12{\cdot}2;$$

or finally by

$$\frac{\mathfrak{M}}{d} = V = x \cdot 11 + y \cdot 5{\cdot}5 + (z - u)\,7{\cdot}8 + u\,12{\cdot}2.$$

In other words, the molecular volume of the compound is obtained by calculating for each carbon atom in the molecule 11 units of volume, for each atom of hydrogen 5·5 units, and for each atom of oxygen either 7·8 or 12·2 units of volume. The value for the atom of oxygen depends on the manner in which it is combined.

Numerous comparisons have shown that oxygen has a specific volume of 7·8 when one of its atoms unites two atoms of carbon together, or unites an atom of hydrogen to an atom

[1] *Ann. Chem. Pharm.* xcvi. 153, 303; c. 19.
[2] *Ibid.* xcvi. 173–185.
[3] In round numbers, C = 12 and O = 16.

of carbon; but when it is attached by both its affinities to the same atom of carbon its volume is 12·2.[1] For example:

Alcohol	$V(C_2H_6O)$	$= 2\cdot 11 + 6\cdot 5\cdot 5 + 7\cdot 8 = 62\cdot 8$
Aldehyde	$V(C_2H_4O)$	$= 2\cdot 11 + 4\cdot 5\cdot 5 + 12\cdot 2 = 56\cdot 2$
Acetic acid	$V(C_2H_4O_2)$	$= 2\cdot 11 + 4\cdot 5\cdot 5 + 12\cdot 2 + 7\cdot 8 = 64\cdot 0$
Ethyl acetate	$V(C_4H_8O_2)$	$= 4\cdot 11 + 8\cdot 5\cdot 5 + 12\cdot 2 + 7\cdot 8 = 108\cdot 0$

Corresponding to the atomic linking expressed by the formulæ—

$CH_3—CH_2—O—H$ Alcohol. $CH_3—CO—H$ Aldehyde. $CH_3—CO—O—H$ Acetic acid.

$CH_3—CO—O—CH_2—CH_3$ Ethyl acetate.

The calculated numbers agree very closely with the observed molecular volumes.[2]

	Molecular Weight $\mathfrak{M}$	B. Pt.	Density at the B. Pt. d	Molecular Volume $V\ \frac{\mathfrak{M}}{d}$
Alcohol . .	$C_2H_6O = 46$	78°	0·736—0·744	61·8— 62·5
Aldehyde .	$C_2H_4O = 44$	21°	0·773—0·786	56·0— 56·9
Acetic acid .	$C_2H_4O_2 = 60$	118°	0·941—0·945	63·5— 63·8
Ethyl acetate	$C_4H_8O_2 = 88$	74°	0·816—0·819	107·4—107·8

This relation of molecular volume to atomic linking enables us to decide in what way the oxygen is combined with the carbon.

Acetone C_3H_6O, at its boiling point, 56°, has the density 0·954—0·957, its molecular volume is therefore 77·3—77·6. But since $3\cdot 11 + 6\cdot 5\cdot 5 + 12\cdot 2 = 78\cdot 2$, and $3\cdot 11 + 6\cdot 5\cdot 5 + 7\cdot 8 = 73\cdot 8$, the volume for O must be taken as 12·2, in order that the calculated and observed molecular volumes may agree. Consequently the oxygen must be united to one carbon atom by both its affinities. The formation and the whole behaviour of acetone correspond to the formula $CH_3—CO—CH_3$, in which

[1] Strictly speaking, the rule should be that the group —CO— has the value 23·2 = 11 + 12·2, leaving it an open question which of the elements causes the increased molecular volume.

[2] H. Kopp, *Ann. Chem. Pharm.* 1855, xcvi. 180.

the group CO occurs. The behaviour of sulphur [1] is similar to that of oxygen.

Buff's [2] investigations show that when two carbon atoms are united together by two affinities they occupy a larger volume than Kopp's law assigns to them. The following molecular volumes are calculated from observations by Kopp and by Buff:—

		Experimental		Calculated	Diff.
Dichloro-ethylene,	$C_2H_2Cl_2$	79·9	K.	78·6	1·3
Ethylene perchloride,	C_2Cl_4	115·4	K.	113·2	5·2
Amylene,	C_5H_{10}	111·2–112·5	B.	110	1·2–2·5
Allyl alcohol,	C_3H_6O	74·6 [3]	B.	73·8	0·8
Ethyl cinnamate,	$C_{11}H_{12}O_2$	211·3	K.	207	4·3
				Mean .	. 2·1
Valerylene,	C_5H_8	103·3–104·9	B.	99	4·3–5·9
Diallyl,	C_6H_{10}	126·7–127	B.	121	5·7–6·0
				Mean .	. 5·5

The volume of all these substances is larger than the theory demands, and the increase is about half as large in the first five substances, in each of which double linking occurs once, as in the case of the two latter, where double linking occurs twice. The larger molecular volume is apparently characteristic of the double linked carbon atoms (=C=C=), but the question requires further investigation.[4] Other polyvalent elements, such as nitrogen,[5] also exhibit similar differences in their specific volumes. When they are united by more than one affinity to one and the same atom they have a

[1] H. Kopp, *Ann. Chem. Pharm.* 1855, xcvi. 305–310.

[2] *Ann. Chem. Pharm.* 1886, Suppl. iv. 143; *Ber. d. deut. chem. Ges.* 1871, 647.

[3] Tollens (*Ann. Chem. Pharm.* 1871, clviii. 104) found 73·9, and T. E. Thorpe (*Chem. Soc. Jour.* 1880, 208) 74·2. Buff (*Ber. d. deut. chem. Ges.* 1871, 648) obtained 72·3 for allyl alcohol containing moisture.

[4] The subject has been recently investigated by Schiff, who confirms Buff's views, but finds the increase for every double linking to be somewhat larger than 2. 'Sui volumi molecolari delle sostanze liquide,' *Accademia dei Lincei*, [3] 1882, xiii.; *Lieb. Ann.* 1883, ccxx. 71. Further the molecular volumes of the aromatic compounds have been found to be smaller than required by theory, whilst, according to Kekulé's formula for benzene (§ 127), they should be somewhat greater.

[5] *Ann. Chem. Pharm.* 1856, c. 19–38.

larger volume than when the affinities are attached to different atoms. That the same atom should occupy different spaces in different compounds is easily explained by the assumption that the atoms forming the molecule do not completely fill the molecular volume with their mass, but, on the contrary, as they are supposed to be in active motion, they require more space than they would actually occupy were they in a state of rest. The atoms are not in a state of rest, but each atom moves about its centre of equilibrium, and the extent of its movements increases with the temperature. When an atom is combined by two or more affinities to the same polyvalent atom, it probably oscillates between the two or more points of equilibrium, to which each of these affinities attempts to attract it. Consequently it requires a larger space for its movements than if it oscillated about a single point of equilibrium, towards which the united forces to which it is exposed attempt to attract it.[1]

§ 139. The position of a monovalent atom also appears to exert a considerable influence on the molecular volume. F. D. Brown[2] has compared primary and secondary propyl iodides, $CH_3—CH_2—CH_2I$ and $CH_3—CHI—CH_3$, at temperatures at which their vapours exert the same pressure, and he has found that the volume of the secondary iodide always exceeds that of the primary iodide by 1·3 to 1·4 per cent. At the temperature of the boiling point, under a pressure of 160 mm., the following results were obtained:

	Density	B. Pt.	Vol.
Primary . . .	1·5867	102·6	107·1
Secondary . .	1·5650	89·9	108·6

The molecular volume, calculated by Kopp's law, gives $V = 3 . 11 + 7 . 5·5 + 1 . 37·5 = 109·0$. T. E. Thorpe[3] and H. Schröder[4] have recently made analogous observations. In 1867 Jungfleisch[5] observed that in the direct substitution

[1] L. Meyer, 'Ueber die Molekularvolumina chemischer Verbindungen,' *Ann. Chem. Pharm.* 1867, Suppl. v. 143.

[2] *Lond. Roy. Soc. Proc.* 1877, xxvi. 238–247.

[3] *Chem. Soc. Journ.* 1880, 102, 141, 327.

[4] *Ber. d. deut. chem. Ges.* 1880, 1560.

[5] Jungfleisch, *Compt. Rend.* 1867, lxvi. 911. Some of the melting points have since been corrected.

of chlorine for hydrogen in benzene, the first, third, and fifth combining chlorine atoms caused a much greater increase in the molecular volumes (determined at the boiling point) than the second, fourth, and sixth. The difference is still greater if the molecular volumes are compared at the melting instead of the boiling points. According to G. Vollmar,[1] the substitution products of ethane exhibit a similar behaviour. The change which is produced in the molecular volumes (measured at temperatures at which the vapour pressures are equal) by replacing H by Cl varies according as the substitution is in the groups $-CH_3$, $-CH_2Cl$, or $-CHCl_2$, so that the isomeric di-, tri-, and tetra-chlorethanes possess different molecular volumes. Similar observations show that in spite of the large amount of material which has been collected, chiefly by the extensive researches of H. Kopp, our knowledge of the relation between molecular volumes and atomic linking cannot by any means be regarded as complete. At the time when Kopp conducted his researches hardly any cases of isomerides possessing very similar properties were known. Nevertheless the molecular volume already forms a very valuable aid in ascertaining the arrangement of the atoms, and we are justified in believing that new investigations would increase its value to a marked extent.

§ 140. The atomic linking of those isomeric bodies which obey Kopp's law, and possess equal molecular volumes at their boiling points, may be indirectly deduced from their specific volume or their density. As a rule, the density of these bodies varies with the temperature to an equal extent,[2] hence a comparison made at a temperature below their boiling points will generally show that the higher boiling compound has the greater density and the smaller molecular volume.

Brühl[3] has recently drawn special attention to the fact that instead of using the boiling points as a means of distin-

[1] Inaug. Diss. Tübingen, 1882; *Ber. d. deut. chem. Ges.* 1882, xv. 2559.

[2] The volume at 0° is generally taken as unity for the coefficients of dilatation. In this case isomerides generally appear to have different coefficients. But there is no difference on comparing the diminution in volume which isomeric bodies undergo on cooling through the same number of degrees from their boiling point.

[3] *Ann. Chem. Pharm.* 1880, cciii. 269.

guishing between isomerides, the densities measured at the same temperature may be employed. Brühl has, however, found one exception to this rule; viz. propyl aldehyde, boiling at 48°, has a greater density at 20° than acetone, which boils at 56·5.[1]

§ 141. It is not only in the case of the carbon compounds that the nature of the atomic linking can be deduced from the specific volumes, although this relation has been very seldom used in the case of inorganic compounds. H. Schröder,[2] in 1840, pointed out that most of the heavy metals and semi-metals increase their volumes on oxidation in proportion to the amount of oxygen combined, so that the difference in the volume occupied by the metal in the oxide and before oxidation is proportional to the quantity of oxygen combined.

Let V(Pb), V(Hg), V(Cu), &c., represent the specific or atomic volumes of the metals, *i.e.* the space occupied by the atomic weights Pb, Hg, Cu, &c., and let V(PbO), V(HgO), &c., represent the volumes occupied by the equivalent weights of the oxides PbO and HgO. Taking the ordinary units in measuring these values, then we obtain their numerical values by dividing the atomic weights of the metals, or equivalent weights of the oxides, by their densities; *e.g.* the specific volumes of lead and of its oxide in the solid state are

$$V(Pb) = \frac{Pb}{d} = \frac{206{\cdot}4}{11{\cdot}38} = 18{\cdot}1$$

$$V(PbO) = \frac{PbO}{d} = \frac{222{\cdot}4}{9{\cdot}4} = 23{\cdot}7$$

Assuming that the volume of the metal remains unaltered by oxidation, then the difference between the two volumes represents the volume of the combined oxygen

$$V(PbO) - V(Pb) = V(O) = 5{\cdot}6.$$

The truth of the hypothesis is rendered highly probable by the following facts:

By applying the same calculation [3] to the oxygen contained

[1] *Loc. cit.* 275. [2] *Pogg. Ann.* l. 553.

[3] The densities required in these calculations are taken from Kopp, *Ueber das spec. Gewicht der chem. Verbindungen* (Frankfurt a. M., 1841), and from

in similar oxides, such as CuO, CdO, ZnO, NiO, HgO, &c., nearly the same value for V(O) is obtained, and also in the case of oxides which contain more than one atom of oxygen to one atom of metal.

$$V(Fe) = \frac{Fe}{d} = \frac{55{\cdot}9}{7{\cdot}8} = 7{\cdot}2$$

$$V(Fe_2O_3) = \frac{Fe_2O_3}{d} = \frac{159{\cdot}7}{5{\cdot}26} = 30{\cdot}4$$

$$V(Fe_2O_3) - 2V(Fe) = 3V(O) = 30{\cdot}4 - 14{\cdot}4 = 16\ ;$$

$$\text{therefore } V(O) = \frac{16{\cdot}0}{3} = 5{\cdot}3.$$

Similar results are obtained for Co_2O_3, Cr_2O_3, Sb_2O_3, and other sesquioxides. These relations indicate that the oxygen in all these oxides is combined in the same way.

This rule does not apply to the specific volumes of all oxides, but for many groups another rule exists. Many metals experience the same change in volume on oxidation, irrespective of the amount of oxygen combined. Thus, in the case of copper,

$$V(Cu) = \frac{Cu}{d} = \frac{63{\cdot}3}{8{\cdot}8} = 7{\cdot}2$$

$$V(CuO) = \frac{CuO}{d} = \frac{79{\cdot}3}{6{\cdot}43} = 12{\cdot}3$$

$$V(Cu_2O) = \frac{Cu_2O}{d} = \frac{142{\cdot}6}{5{\cdot}75} = 24{\cdot}8$$

Reducing these numbers to the same quantity of metal, we obtain:

$$V(Cu_2O) - V(Cu_2) = 24{\cdot}8 - 14{\cdot}4 = V(O) = 10{\cdot}4$$
$$V(Cu_2O_2) - V(Cu_2) = 24{\cdot}6 - 14{\cdot}4 = V(O_2) = 10{\cdot}2 = 2 \,.\, 5{\cdot}1$$

Two atoms of oxygen in cupric oxide occupy the same volume as one atom in cuprous oxide. The same is true of the oxides of mercury and silver.

Bödeker, *Die Beziehungen zwischen Dichte und Zusammensetzung bei festen und liquiden Stoffen* (Leipzig, 1860).

In many of the higher oxides the difference of five units of volume is produced by two atoms instead of by one; *e.g.*

$$V(SnO_2) - V(Sn) = \frac{149{\cdot}7}{6{\cdot}96} = \frac{117{\cdot}8}{7{\cdot}29} = 21{\cdot}5 - 16{\cdot}1$$
$$= V(O_2) = 5{\cdot}4.$$

The compounds of the lighter metals and of the non-metallic elements exhibit quite different relations. If this subject of specific volumes was investigated afresh, there is no doubt that it would permit of numerous conclusions being drawn as to the nature of the atomic linking in various compounds.

§ 142. Many other physical properties of chemical compounds also depend on the atomic linking, so that these properties may be used for deducing the latter. But this is not true of all physical properties; on the contrary, they may be divided into two sharply defined groups, viz. those depending solely on the nature of the atoms of which the compound is composed, and those which depend not only on the nature of the atoms but also on the position or manner in which the atoms are arranged.[1] At present it is not yet possible to arrange all properties into these two groups. The refractive power of chemical compounds is chiefly dependent on the nature of the atoms, but it is also influenced to a certain extent by the atomic linking. It has been already mentioned in § 72 that Landolt and Gladstone[2] found that the refractive power of certain organic compounds cannot be represented by the sum of their refraction equivalents. At the suggestion of Landolt, Brühl[3] carefully examined a large number of these compounds, and found that the refraction equivalent of the polyvalent atoms depends on the manner in which they are combined; the refraction equivalent of the monovalent atoms is independent of their arrangement. If the molecular refraction of all organic compounds could be

[1] The colours of compounds appear to be determined by the nature of certain of their elementary constituents alone. The observations of Witt (*Ber. d. deut. chem. Ges.* 1876, ix. 522), of Liebermann (*ibid.* 1880, xiii. 913), and, amongst others, of Krüss and Oekonomides (*ibid.* 1883, xvi. 2051) appear to indicate the existence amongst organic compounds of a connection between the colour and atomic linking.

[2] Landolt, *Pogg. Ann.* 1864, cxxiii. 603; Gladstone, *Ber. d. deut. chem. Ges.* 1870, ccxlvii. 369. [3] *Ann. Chem. Pharm.* 1880, cc. 139; cciii. 1 and 255.

represented as the sum of the refraction equivalents of the atoms, then a difference of H_2 in the composition would make a difference of $2Rf(H) = 2 . 1{\cdot}29 = 2{\cdot}58$ units in the molecular refraction. This is approximately true for certain classes of bodies, especially for alcohols, aldehydes, and ketones, containing the same number of carbon atoms. Let A be Cauchy's constant independent of wave length, and D the density at 20°, compared with water at 4°; then we have the following differences for H_2:

	$\mathfrak{M}$	$\frac{A-1}{D}\mathfrak{M}$	Diff.
Ethyl alcohol	C_2H_6O	20·31	2·14
Aldehyde	C_2H_4O	18·17	
Propyl alcohol	C_3H_8O	28·00	2·45
Acetone	C_3H_6O	25·55	
Norm. butyl alcohol	$C_4H_{10}O$	35·45	2·59
Norm. butyl aldehyde	C_4H_8O	32·86	
Methylhexyl carbinol	$C_7H_{16}O$	65·57	2·28
Methylhexyl ketone	$C_7H_{14}O$	63·29	

and similar differences for analogous compounds.

But the following bodies exhibit much smaller differences:

I.	II. $\mathfrak{M}$	III. $\frac{A-1}{D}\mathfrak{M}$	IV. Diff.	V. $\Sigma Rf A$	VI. Diff.
Propyl alcohol	C_3H_8O	28·00	0·91	25·22	1·87
Allyl alcohol	C_3H_6O	27·09	0·90		
Isopropyl alcohol	C_3H_8O	27·99			
Propyl aldehyde	C_3H_6O	25·42	0·11	22·64	2·67
Acrolein	C_3H_4O	25·31	0·24		
Acetone	C_3H_6O	25·55			
Propyl chloride	C_3H_7Cl	33·36	0·73	30·56	2·07
Allyl chloride	C_3H_5Cl	32·63			
Propylethyl ether	$C_5H_{12}O$	42·86	0·66	40·10	2·10
Allylethyl ether	$C_5H_{10}O$	42·20			
Propyl acetate	$C_5H_{10}O_2$	43·11	0·90	40·42	1·79
Allyl acetate	$C_5H_8O_2$	42·21			
Amylene	C_5H_{10}	39·29	0·64	37·40	2·09
Valerylene	C_5H_8	38·65		34·62	4·03

Double linking of the carbon atoms is exhibited by all the ompounds which contain less than the maximum number of nonovalent elements. They all possess molecular refractions onsiderably greater than the sum of the values of their refrac- ion equivalents as given in § 72. These calculated values re contained in column V. of the above table. From these nd similar observations Brühl arrived at the conclusion that he double linking of the carbon atom increases the molecular efraction. From a large number of observations, he found he mean increase to be two units for each pair of doubly inked carbon atoms. The above table shows that the de- rease of 2·58 units produced by the loss of two hydrogen toms is counterbalanced to the extent of four-fifths by the louble linking of the carbon atoms.

The conclusion that double linking was the cause of this difference would be open to doubt if the observation had only been made in the case of allyl compounds. But amylene C_5H_{10}, belonging to the series C_nH_{2n}, which requires two more hydrogen atoms in order to convert it into a saturated com- pound, also exhibits the same increase, and valerylene and diallyl, of the type C_nH_{2n-2}, which require four atoms of hydrogen for conversion into saturated compounds, and in which, therefore, double linking occurs twice, exhibit double his difference, viz. four units.

A superficial observation might lead to the conclusion hat the refractive power of benzene and its homologues of he type C_nH_{2n-6}, which are relatively four atoms poorer in hydrogen than diallyl, and which require eight atoms of hydro- gen for saturation, would exceed the calculated value by eight units. This is, however, not the case.

I.	II. $\mathfrak{M}$	III. $\frac{A-1}{D}\mathfrak{M}$	IV. $\Sigma R_f A$	V. Diff.
Diallyl . . .	C_6H_{10}	45·99	42·06	3·93
Benzene . .	C_6H_6	42·16	39·90	5·26
Toluene . . .	C_7H_8	50·06	44·34	5·72
Mesitylene . .	C_9H_{12}	65·22	59·22	6·00

The optical behaviour of the hydrocarbons C_nH_{2n-6} indicates three, and not four, double linkings. This is an excellent confirmation of Kekulé's hypothesis (§ 127) on the atomic linking of benzene and its derivatives. The seventh and eighth affinities, which are not absolutely required to maintain the coherence of the chain, serve to close the ring: thus only three double linkings can exist.[1]

After Brühl had observed similar behaviour in numerous examples of aromatic compounds, he investigated the influence of the single and double linking of oxygen to carbon on the molecular refraction. After comparing large series of compounds containing the groups $=C=O$ and $-\overset{|}{C}-O-\overset{|}{}$, he arrived at the conclusion that the double linking of oxygen causes a small increase in the molecular refraction, but that the influence of monovalent elements remains the same under all circumstances.[2] If the atoms singly linked are denoted as Brühl suggests by O′ and C′, and the atoms united to carbon by double linking are represented by O″ and C″, the following values are obtained for the refraction equivalents of these elements, and must be substituted for those in § 72.

Element.	R'_A.	R''_A.
O′ . . .	2·71 . . .	2·8
O″ . . .	3·29 . . .	3·4
S′ . . .	13·53 . . .	14·10
S″ . . .	15·09 . . .	15·61
C′ . . .	4·86 . . .	5·06
C″ . . .	5·86 . . .	6·075
(C=C) . .	11·72 . . .	12·15
(C=O) . .	8·15 . . .	8·46
(CH_2) . . .	7·44 . . .	7·60

Since the value of the refraction equivalent is increased by two for each pair of double linked atoms and by 0·58 by the doubling of O to C, the molecular refraction of ethyl-hydrocinnamate, $C_6H_5—CH_2—CH_2—CO—O—CH_2—CH_3$ = [illegible] 3·52

[1] The refractive power of sulphur is similarly affected (*Ber.* xv. 2878).

The calculated value is

$$\frac{A-1}{D}\mathfrak{M} = 11.4{\cdot}86 + 14.1{\cdot}29 + 2.\ 2{\cdot}71 + 3.2{\cdot}00 + 0{\cdot}58 = 83{\cdot}52$$

or $$= 3.11{\cdot}72 + 8{\cdot}15 + 4.7{\cdot}44 + 2{\cdot}71 + 6.1{\cdot}29 = 83{\cdot}52.$$

Brühl has shown that the two different refraction equivalents of oxygen can be of service in determining atomic linking; take the case of paraldehyde as an example.

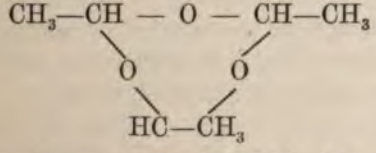
If three molecules of aldehyde C_2H_4O, on polymerisation, simply unite together forming $C_6H_{12}O_3$, then the molecular refraction of paraldehyde would be three times that of aldehyde, viz. $3 \times 18{\cdot}15 = 54{\cdot}54$ if we take the observed values for aldehyde, or $3 \times 18{\cdot}17 = 54{\cdot}51$ if we take the calculated; but in reality a much smaller value is obtained:

$$\frac{A-1}{D} \cdot \mathfrak{M} = 52{\cdot}48.$$

The same result is obtained if Rf $(\acute{O}) = 2{\cdot}71$ is used instead of Rf $(\ddot{O}) = 3{\cdot}29$ in the calculation.

$$\frac{A-1}{D}\mathfrak{M} = 6\ .\ 4{\cdot}86 + 12\ .\ 1{\cdot}29 + 3 \times 2{\cdot}71 = 52{\cdot}77.$$

This confirms the accuracy of the views held by Erlenmeyer,[1] and by Kekulé and Zincke,[2] that the three aldehyde molecules in paraldehyde are linked together by their oxygen atoms forming a ring,



The propargyl compounds, in which the radical propargyl with a treble carbon linking,

$$C_3H_3 = H{-}C{\equiv}C{-}CH_2{-}^*,$$

was formerly supposed to exist, exhibit a peculiar behaviour.

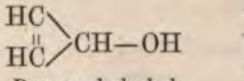
The following table shows that the values for the refractive power of these compounds do not exhibit a greater deviation

[1] *Lehrbuch der org. Chem.* 1868, p. 307.
[2] *Ber. d. deut. chem. Ges.* 1870, 471.

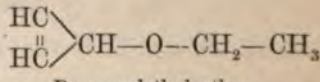
than the allyl compounds do from the values in column V., which are calculated without assuming the existence of double linking.

I.	II. $\mathfrak{M}$	III. $\frac{A-1}{D}\mathfrak{M}$	IV. Diff.	V. $\Sigma R_f A$	VI. Diff.
Propyl alcohol .	C_3H_8O	28·00	0·91	27·61	0·39
Allyl alcohol .	C_3H_6O	27·09	3·08	25·03	2·06
Propargyl alcohol .	C_3H_4O	24·01		22·45	1·56
Propylethyl ether .	$C_5H_{12}O$	42·86	0·66	42·49	0·40
Allylethyl ether .	$C_5H_{10}O$	42·20	2.70	39·91	2·29
Propargylethyl ether.	C_5H_8O	39·50		37·33	2·23
Propyl acetate .	$C_5H_{10}O_2$	43·11	0·90	43·20	−0·09
Allyl acetate . .	$C_5H_8O_2$	42·21	2·50	40·62	1·59
Propargyl acetate .	$C_5H_6O_2$	39·71		38·04	1·67

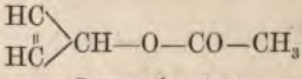
From these results Brühl concludes that there is only *one double* linking in the propargyl compounds.



Propargyl alcohol.

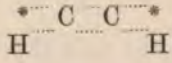


Propargylethyl ether.



Propargyl acetate.

The objection to this view is that the strong resemblance in the properties of the propargyl compounds and those of acetylene can no longer be represented by analogous formulæ, unless the existence of two free affinities in acetylene instead of a treble carbon linking is assumed, thus ;

 instead of $H-C\equiv C-H$

§ 143. In many cases, conclusions may be drawn regarding the atomic linking from the thermal phenomena which accompany the formation and decomposition of compounds. Recently Julius Thomsen [1] has made the important discovery that single and double linking of the carbon atoms may be

[1] *Ber d. deut. chem. Ges.* 1880, 1321, 1328, 1806 and 1810; *Liebig's Annalen*, 1880, ccv. 133.

distinguished by means of the heat of combustion of the hydrocarbons. Thomsen's investigations confirm the generally accepted formulæ for

CH_4	$H_3C—CH_3$	$H_3C—CH_2—CH_3$
Methane.	Ethane.	Propane.
$HC \equiv CH$	$H_2C = CH_2$	$H_2C=CH—CH_3$
Acetylene.	Ethylene.	Propylene.

But they lead to the conclusion that benzene, C_6H_6, is held together by nine simple linkings and not by three double and three single linkings, as is assumed to be the case in Kekulé's hypothesis.

Brühl's optical researches confirm Kekulé's formula[1] (§ 127) No. I., but Thomsen's results are in favour of formulæ IV. or V. This contradiction can only be explained by renewed investigation in each subject.

Capacity for heat belongs to the group of properties which depend chiefly on the nature of the atoms; it is however also influenced by the atomic linking, inasmuch as this determines the state of aggregation and other properties of the substance.[2] The latent heat of vaporisation and the latent heat of fusion[3] (which are closely allied to the specific heat) and many other physical properties depend not only on the nature of the atoms but also on their arrangement. Our knowledge of these relations is only in the first stage of its development. But it is probable that the present incomplete knowledge of the connection between the composition of compounds and their physical and chemical properties will rapidly increase and develop, forming a special department having for its aim the representation of the properties of chemical compounds as functions of the mode of combination and of the nature of the atoms contained in them.

A general investigation of the mutual relations between composition and properties will correct and strengthen our insight into the laws of atomic linking and will rapidly bring us nearer to the goal which a few years ago many chemists had declared to be unattainable.

[1] See § 142. [2] A. v. Reiss, *Wied. Ann.* 1881, xiii. 477.
[3] Person, *Ann. Chim. Phys.* [3] xxi. 24, 27.

The investigation of the relation of the atoms to one another is a difficult problem, and one which requires great caution. In its solution we shall encounter and have to correct many errors; but although we have only reached the very commencement, we can clearly perceive that the problem is one which will not surpass human powers.

VIII.

MOLECULAR WEIGHT AND ATOMIC LINKING OF BODIES, TO WHICH AVOGADRO'S HYPOTHESIS CANNOT BE APPLIED.

§ 144. THE preceding speculations on atomic linking depend on the supposition that the molecular weights of the compounds as well as the atomic weights of their constituents are known. But at present this condition is only fulfilled by a small number of the chemical compounds which have been prepared and investigated. Avogadro's rule for determining the molecular weight cannot be applied to the large majority of compounds, since they either do not volatilize without decomposition, or they only volatilize at temperatures which are too high to permit of the determination of their density in the state of vapour or gas.

The difficulty of solving the problem of the constitution of these compounds is greatly increased by this deficiency, and consequently our knowledge of the constitution of these bodies suffers perceptibly. There is a tendency to apply the laws which have been discovered in the investigation of gaseous bodies to non-gaseous substances, and this is permissible to a certain extent, but the application of rules which are valid for gases and vapours to liquids and solids has already led to mistakes in more than one instance, and therefore great caution is necessary in order to avoid such errors. The attempt was first made by Avogadro, who arbitrarily assumed the molecular weights of non-gaseous bodies and attempted to deduce the atomic weights of non-volatile elements from these molecular weights. The assumptions he made and the deductions he drew from them were unfortunate. When they were afterwards shown to be incorrect they brought

discredit on his views, otherwise correct. Gerhardt was scarcely more successful. He introduced Avogadro's hypothesis into his system, thus giving it again its due position. He also deduced from the molecular weights of gases and vapours the molecular weights of their non-volatile compounds, and from these, again, atomic weights, especially in case of the metals; and obtained thus atomic weights which were generally incorrect. At the present time it is a common error to apply without due consideration laws which are valid for the gases to non-gaseous bodies; it is not, however, the atomic weights alone which are incorrectly determined in this way, but the power of saturation of the atoms is frequently deduced from arbitrarily chosen molecular weights by applying principles which can only be applied to molecular weights which have been actually determined. Since the discussion on molecular weights ceased, a bad habit has crept into the textbooks of omitting the statement of the vapour density, so that the reader no longer knows whether the molecular weight which is accepted by the author is hypothetical or whether it has been determined experimentally. In this way hypotheses acquire the appearance of facts.

§ 145. The difference between the gaseous state and the other states of aggregation is too great to allow rules which are valid in the case of the former to be applied without further ceremony to the latter.

With the exception of the molecular weight or total mass of the molecule, no other quantity depending on the nature of the molecule has, as a rule, any influence on the physical properties of the gases. The physical phenomena which are exhibited by gaseous bodies appear to depend chiefly and essentially on the rectilinear progressive motion of the molecule, on which the peculiarity of the gaseous state of aggregation also depends. This rectilinear motion is determined not only by the temperature but also by the mass of the molecules.

It has already been stated (§§ 13, 14, 15) that the square of the velocity of this motion is proportional to the absolute temperature and inversely proportional to the molecular weight; for equal temperatures, the velocities of the molecules

of two gases are inversely as the square roots of their densities. The constitution and the material nature of the molecules only exert a subordinate influence on the motion of the molecules and on the visible properties of gases.

The vapour pressure undoubtedly depends on the mutual attraction of the molecules, on their nature, their internal forces, and, consequently, on the arrangement of the atoms contained in them. The latter especially affects the chemical changes, the decomposition, and the formation of the molecules. These are therefore the only properties which can yield information concerning the nature of the atomic linking in the molecules of gases.

The case is different for liquid and solid bodies. Here the external physical properties depend essentially on the nature of the atomic linking in the molecules. Although our knowledge of this relation has scarcely passed the first stage of its commencement, we are however acquainted with a whole series of properties which enable us to arrive at conclusions regarding atomic linking; the present views on the constitution of many bodies have indeed to a great extent been derived from their properties in the liquid or solid state.

This wide difference between the different states of aggregation appears to be chiefly due to the fact that in the mass of a gas or vapour which is diffused through a relatively large space, the particles are on an average so far apart that they cease to exert any action on each other, whilst in both the other states of aggregation each particle is so close to its neighbours, that they act energetically on each other. The effect of the mutual attractions is visible in cohesion, crystallisation, and other phenomena. Since it is obvious that these actions take place beyond the limits of the molecule, it is clear that we are not justified in regarding without further question each of these effects as solely and entirely due to the same causes by which the coherence of the molecule in the gaseous state is produced. On the other hand, there is no reason for assuming that the forces which maintain the internal coherence of the molecule in the gaseous state, should cease to be effective in the other states of aggregation. It is only probable in this case that other molecular forces are also present. How

far their assumption is necessary can only be decided by a theory which advances abreast with experimental observation.

§ 146. In determining the constitution of those bodies which can exist in the state of gas or vapour, we start from the small unit of mass called a molecule. The question arises whether the supposition of discrete particles of matter composed of a definite number of atoms is necessary or even permissible for the liquid or solid state.

The reasons arising from chemical and physical observations which require the discontinuity of matter hold good for all three states of aggregation. In each of these states the mass of the chemical elements and compounds must be regarded as composed of particles of matter which are separated from each other by intervening spaces. These particles of matter are not atoms; at least, not in all cases, since it is not merely the number and nature of the atoms in the composition of a substance, but also the manner in which the atoms are united together, which is characteristic of the different bodies. If this were not the case, isomerides—*i.e.* combinations of the same constituents arranged dissimilarly—could not exist and preserve their peculiar properties in the changes through the different states of aggregation. That this really is the case compels us to assume that certain groups of atoms or molecules, which are characteristic of the nature of the substance, also exist in the liquid and solid state. In liquids these molecules move about with a certain amount of freedom, whilst in solids they occupy certain mutual points of equilibrium, about which only a limited movement is possible. In the liquid state the molecule can be defined as that system whose particles remain connected during the internal movements of the liquid, such as those taking place during diffusion and transpiration.

This sharp characteristic is wanting in the solid state, and the supposition of definite isolated particles of matter only appears to be justified if certain groups of atoms separate themselves from the rest, either by a greater distance or by undergoing a common movement. It is very clear that in such an arrangement of the atoms of the four elements,

A, B, C, D, as the following, molecules could not be fairly assumed to exist:—

A B C D A B C D A B C D . . . .
C D A B C D A B C D A B . . . .
A B C D A B C D A B C D . . . .
C D A B C D A B C D A B . . . .

But the mass may fairly be said to consist of molecules of the composition $\frac{AB}{CD}$ in an arrangement similar to the following:

AB	AB	AB	AB
CD	CD	CD	CD
AB	AB	AB	AB
CD	CD	CD	CD

Which of these schemes most correctly represents the majority of existing solid bodies cannot be immediately decided. Probably the latter, as many physical phenomena appear to indicate that most solid bodies contain empty spaces between their particles. The spaces are very large in comparison with that which the material particles really occupy, and it is not probable that there are large spaces between the atoms united together by chemical affinity. It may therefore be assumed that the atoms are not uniformly dispersed through the entire space, but that they are united to molecules, and these molecules are separated from each other by larger spaces. If speculations of this nature lead us to regard chemical substances in each of the three states of aggregation as composed of molecules, we must not forget that this hypothesis is scarcely so firmly founded in the case of liquids, and certainly not in the case of solids, as it is for gaseous bodies. At present, at least, the notion of the molecule cannot be as sharply defined for the liquid and solid state as it can be for the gaseous state by the aid of Avogadro's hypothesis.

§ 147. The molecular weights of a certain substance need not be the same in different states of aggregation. It is not even probable that this is the case. On the contrary, a large number of observations indicate that substances in the gaseous state frequently possess molecules having a different composition from those in the liquid or solid state.

It has already been mentioned, in §§ 18, 25, 33, and elsewhere,[1] that many substances, in the state of gas or vapour, exhibit two different molecular weights, according to the temperature—*e.g.* for sulphur, S_6 and S_2; for nitrogen peroxide, N_2O_4 and NO_2; for ozone, probably O_3; for ordinary oxygen, O_2. The larger molecular weight always corresponds to the lower temperature, and can be changed to the smaller by raising the temperature.

This change is often to be observed by the eye in the external properties; in nitrogen peroxide, for example, by the dark red colour the vapour assumes when the molecules N_2O_4 split up into two new molecules, NO_2. As this splitting up is accompanied by a change of properties, it must be regarded as the conversion of the substance into an allotropic modification with a smaller molecular weight, or, in other words, the compound whose molecules are represented by N_2O_4 is not identical but polymeric with that whose molecules are represented by the formula NO_2.

Among liquid and solid bodies cases also occur in which a rise in temperature changes one modification of the substance into another without altering its composition—*e.g.* red phosphorus into colourless, metaldehyde and even paraldehyde (in presence of a small quantity of sulphuric acid) into ordinary aldehyde, solid chloral into liquid, cyanuric acid into cyanic, &c. In many cases a determination of the vapour density proves that the molecular weight is changed. For example, the molecular weight of paraldehyde, $C_6H_{12}O_3$, is three times that of aldehyde, C_2H_4O. In other cases a similar change is probable, although it cannot be proved by Avogadro's law.

Hence it follows that we are not justified without further consideration in regarding the molecular weight determined for a substance in the gaseous state, as valid for the same substance in the liquid or solid state. But, so far as our experience goes, the molecular weight in the liquid and solid states is never smaller, but may be many times larger, than in the gaseous state. Several molecules may unite to form a single molecule when a gas or vapour condenses; but no case has been observed where one molecule splits up into two or

[1] These cases will be again referred to in Part iii.

three. Such a decomposition frequently occurs when an increase in temperature transforms a liquid or solid to the gaseous state.

§ 148. The methods for determining the molecular weight in the liquid or solid state are at present undeveloped. There appears to be no doubt that the determination is possible, but scarcely any thorough attempt has been made to carry it out.

In the case of those bodies the molecular weights of which have been determined for the gaseous state, it is customary to regard these values as valid for each of the other states of aggregation. By this means too high a value is avoided; but in many cases the accepted number is too small, and only represents a fraction of the real molecular weight.

Another custom, which is even more arbitrary and less justifiable, is to deduce from the molecular weight of a compound determined in the gaseous state the molecular weight of a second compound, which is derived from or can be converted into the first compound, by replacing one or more of its atoms or radicals by others. The molecular weight given to the second compound is made to correspond as closely as possible to that of the first. The new atoms or radicals take the position which was occupied by the atoms they have replaced. In this way the molecular weights of the salts of an acid are deduced from the known molecular weight of the acid, and the molecular weights of non-volatile acids from their volatile ethereal salts. For according to our present views (which are somewhat different from the dualistic ideas) salts are formed from acids by the replacement of their so-called 'basic' or 'typical' hydrogen by atoms of metals or by compound radicals.

Thus, from the molecular weight of hydrochloric acid, which is represented by HCl, the molecular weights of its salts are deduced; *e.g.*

NaCl, KCl, AgCl, &c.

From the molecular weight of acetic acid, $C_2H_4O_2$, the molecular weights of the corresponding acetates follow; *e.g.*

$NaC_2H_3O_2$, $KC_2H_3O_2$, $AgC_2H_3O_2$, &c.

The molecular weights of boric, oxalic, and silicic acids cannot be determined by Avogadro's rule, but the vapour densities of their ethereal salts have been found to be 5·14, 5·1, and 7·23, corresponding to the molecular weights, $BO_3(C_2H_5)_3 = 145·7$, $C_2O_4(C_2H_5)_2 = 145·7$, $SiO_4(C_2H_5)_4 = 207·6$.

By substituting an atom of hydrogen for each ethyl radical, the molecular weights generally accepted for the acids are obtained, thus;

$$BO_3H_3 = 61·9, \qquad C_2O_4H_2 = 89·8, \qquad SiO_4H_4 = 95·8.$$

If the hydrogen of an acid is not, as in these cases, replaced by monovalent, but by polyvalent, atoms or radicals, then it is assumed that several molecules are linked together to form a single molecule, a by no means unfrequent occurrence with gaseous compounds.

Thus 2HCl forms $CaCl_2$, $ZnCl_2$,

$2C_2H_4O_2$ forms $Ca(C_2H_3O_2)_2$, $Zn(C_2H_3O_2)_2$, &c.

If the acid molecule contains more than one replaceable atom of hydrogen, doubt may arise when these are saturated by polyvalent metals. Thus the molecular weight of anhydrous calcium oxalate may be represented by

$$C_2O_4Ca, \text{ or } C_2O_4\left\{\begin{matrix}Ca\\Ca\end{matrix}\right\}C_2O_4 = (C_2O_4)_2Ca_2,$$

or by

$$\begin{matrix}C_2O_4-Ca-C_2O_4\\ |\qquad\quad |\\ Ca-C_2O_4-Ca\end{matrix} = (C_2O_4)_3Ca_3,$$

according as we consider the atoms of hydrogen replaced by the divalent calcium atom to belong to one or to two different molecules.

§ 149. An acquaintance with the atomic weights of the elements and with their power of saturation is necessary in speculations of this kind. In the preceding paragraphs it is assumed that the molecular weight of one of the compounds related to the substance in question is known. In many cases, however, this is not requisite, if the laws which hold good for molecules of gaseous bodies are directly applied to liquid and solid bodies.

Assuming the validity of these laws in each of the states of aggregation, the molecular weight of many compounds can be determined by applying the rules laid down in §§ 100–103, especially by the rule that the number of monovalent atoms contained in a molecule cannot be greater than $n_1 = n_3 + 2n_4 + 3n_5 + 4n_6 + 2$, where n_1, n_3, &c., have the values assigned to them in § 103. It is very difficult to decide whether the indispensable condition, in applying this rule—viz. that not only the quantitative composition of the given compound should be known, but also the capacity of saturation of all the atoms contained in it—is fulfilled or not in a given case. It is uncertain whether the valency of the given element in the gaseous state, which can be determined without any special difficulty when a large number of its gaseous compounds are known, remains unchanged in the other states of aggregation. We shall see that this must be left an open question in the case of many elements, whilst other elements appear to have the same valency in the several different states of aggregation.

§ 150. Assuming that the powers of saturation are given, then, for compounds composed entirely of monovalent elements, $n_3 = o$, $n_4 = o$, $n_5 = o$, $n_6 = o$; therefore, $n_1 = 2$, or the molecule of this compound can only contain two atoms. According to this rule the molecular formulæ for the following compounds will be

KCl	NaCl	LiCl	AgCl	AgAg	NaNa
Potassium chloride.	Sodium chloride.	Lithium chloride.	Silver chloride.	Silver.	Sodium.

The only possible objection to these formulæ is that the elements contained in these compounds are only apparently and not really monovalent. This question is discussed in the following pages. It is also possible, in the case of the metals, that their molecules consist of a single atom, like the molecule of mercury vapour.

For compounds of di- and mono-valent elements, $n_3 = o$, $n_4 = o$, $n_5 = o$, $n_6 = o$; therefore, $n_1 = 2$. The maximum value of the molecular weight is therefore represented by that analytical quantity which contains only two monovalent atoms.

On the assumption that Cl and I are monovalent, and S and Se divalent, we have molecular weights represented by the following formulæ:

Chloric acid, $HClO_3$.
Sulphuric acid, H_2SO_4.
Acid potassium sulphate, $HKSO_4$.
Neutral potassium sulphate, K_2SO_4.
Pyrosulphuric acid, $H_2S_2O_7$.
Iodic anhydride, I_2O_5.
Selenious acid, H_2SeO_3.
Acid potassium sulphite, $HKSO_3$.
Sodium selenite, Na_2SeO_3.
Potassium chlorosulphonate, KSO_3Cl.

For compounds of mono-, di-, and tri-valent elements, the maximum value is given by the equation $n_1 = n_3 + 2$. Hence we have the following molecular formulæ:

Boric acid, H_3BO_3.
Phosphoric acid, H_3PO_4.
Pyrophosphoric acid, $H_4P_2O_7$.
Hydroxylamine, H_3NO.
Dihydric potassium phosphate, KH_2PO_4.
Silver arsenate, Ag_3AsO_4.

The maximum value for compounds containing tetravalent atoms is determined by the equation, $n_1 = n_3 + 2n_4 + 2$, which is fulfilled by the following molecular formulæ:

Potassium silicate, K_4SiO_4.
Sodium silicate, Na_4SiO_4.
Tetrabasic silicic acid, H_4SiO_4.
Hexabasic silicic acid, $H_6Si_2O_7$.

In any attempt to double or multiply these formulæ, we should have

$$n_1 > n_3 + 2n_4 + 2;$$

therefore the conditions required for the existence of the molecule would cease; *e.g.*

Na_2Cl_2	$n_1 = 4$,	consequently	$n_1 > 2$
$H_4S_2O_8$	$n_1 = 4$	,,	$n_1 > 2$
$H_6B_2O_6$	$n_1 = 6$	,,	$n_1 > n_3 + 2 = 4$
$H_8Si_2O_8$	$n_1 = 8$	,,	$n_1 > 2n_4 + 2 = 6$.

These molecular weights are incorrect, if we assume that the conditions for the existence of the molecule in the liquid and solid state are the same as those which hold good

for the gaseous state, and, secondly, that the atoms really possess the valency ascribed to them. In certain cases, however, no conclusion as to the molecular weight can be drawn from the capacity of saturation of the atoms, even under these conditions, viz. whenever $n_1 \leqq n_3 + 2n_4 + 3n_5 + 4n_6$. Thus each of the following formulæ for metaphosphoric acid and dibasic silicic acid satisfies the conditions for the molecular weight, since $n_1 = n_3$ or $n_1 = 2n_4$

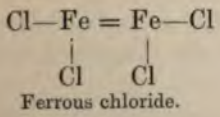
HPO_3,	$H_2P_2O_6$,	$H_3P_3O_9$,	$H_4P_4O_{12}$, &c.
H_2SiO_3,	$H_4Si_2O_6$,	$H_6Si_3O_9$,	$H_8Si_4O_{12}$, &c.

Several modifications of metaphosphoric acid are really known, which perhaps correspond to the above formulæ.

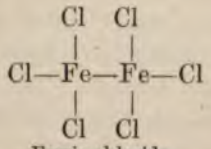
No conclusion can be drawn regarding the molecular weight of a compound composed entirely of polyvalent atoms. Thus the molecular weight of the oxides of divalent metals which is generally represented by the smallest empirical formula, ZnO, HgO, &c., may quite as well be represented by a multiple of these quantities, Zn_2O_2, Zn_3O_3, $Hg_2O_2Hg_3O_3$.

§ 151. We are, as a rule, justified in assuming that the compound does not contain unsaturated affinities. In this case the minimum value of the molecular weight of many compounds may be determined with the aid of a knowledge of the capacity for saturation of the atoms.

Thus the rational formula, $FeCl_2$, for ferrous chloride cannot represent the molecular weight, because the existence of ferric chloride with the molecular weight, Fe_2Cl_6, shows that the atom of iron contains at least four affinities. If none of these affinities are unsaturated, the molecular weight of ferrous chloride must be at least Fe_2Cl_4, it must contain at least two atoms of iron, which mutually saturate part of their affinities. Thus we have

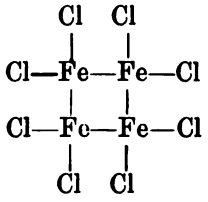


Ferrous chloride.



Ferric chloride.

But the molecular weight of ferrous chloride may just as well be Fe_3Cl_6, Fe_4Cl_8, or any other multiple of $FeCl_2$; *e.g.*



Which of these possible formulæ is correct cannot be decided from the capacity of saturation (see p. 288).

It is scarcely necessary to mention that in this state of affairs it is not only permissible but also very advisable in representing chemical reactions to use the simplest rational formulæ instead of unknown molecular weights.

The action of hydrochloric acid on iron and the conversion of ferrous chloride into ferric may without hesitation be represented by the equations

$$Fe + 2HCl = FeCl_2 + HH \text{ and } FeCl_2 + Cl = FeCl_3.$$

It must, however, not be forgotten that these formulæ do not denote molecular weights. The common custom of using as the formula for ferric chloride the molecular weight in the gaseous state Fe_2Cl_6, and for ferrous chloride the formula $FeCl_2$, which obviously represents a much smaller quantity than the molecular weight, is illogical and very objectionable. If Fe_2Cl_6 is taken, then Fe_2Cl_4 should be used, and if $FeCl_2$ is employed, $FeCl_3$ should be used. If this is not done, the conversion of ferric chloride into ferrous appears to be accompanied by a splitting up of the molecule, whereas it is highly probable that in reality the reverse takes place. When the double atoms of Berzelius $\dot{C}l = Cl_2$ were in use, the simplest formulæ were $Fe\dot{C}l = FeCl_2$ and $\dot{F}e\dot{C}l_3 = Fe_2Cl_6$, but since the double atoms have been discarded the simplest formulæ are $FeCl_2$ and $FeCl_3$.

§ 152. A molecular weight deduced from the capacity of saturation of the atoms is always uncertain and requires confirmation.

The investigation of the physical properties of bodies can alone yield a method for arriving at a trustworthy determination of the molecular weight.

The greater or lesser degree of volatility affords us aid in the case of those substances which, though volatile, only volatilise at temperatures which are so high that our methods for determining the density are unavailable.

Numerous observations have shown that volatility depends not only on the nature of the substance, but also on the magnitude of its molecular weight. As far as is known at present volatility appears to increase as the molecular weight diminishes, other conditions being equal. It also depends not only on the number and nature of the atoms contained in the compound, but also on the manner in which they are arranged. The influence of the atomic linking is perceptible in that class of isomerides known as metamerides, viz. substances having the same constituents and the same molecular weight, but a different arrangement of the atoms. For example, ethylene chloride $ClH_2C—CH_2Cl$ is less volatile than ethylidene chloride $H_3C—CHCl_2$; the former boils at 84° under the ordinary atmospheric pressure, and the latter at 58°; acetic acid and each of its homologues of the formula $C_nH_{2n}O_2$ boils (on an average) 82° higher than the metameric ethereal salt having the same molecular weight and the same formula.[1]

Owing to the influence of atomic linking on the volatility of compounds, the knowledge of the dependence of volatility on the molecular weight can only be used in the comparison of compounds of similar or analogous constitution. But this comparison can be made in many series of compounds, and it is always seen that for two analogously constituted compounds the one with the lower molecular weight is the more volatile. This fact is frequently used in organic chemistry in order to determine the molecular weight approximately.

The influence of the molecular weight also makes itself felt even where the constituents differ in quality and quantity, and are not quite similarly arranged. In many cases the increase of the volatile constituents in a compound often lowers the boiling point in spite of the increased molecular

[1] H. Kopp, *Ann. Chem. Pharm.* l. 128, xcvi. 6.

weight. Thus the hydrocarbon C_nH_{2n} becomes more volatile when it is converted into C_nH_{2n+2} by the addition of H_2. In other cases the increase in the molecular weight is the preponderating influence. Perchlorethylene, C_2Cl_4, boils at 122°, whilst its compound with chlorine, perchlorethylene chloride, C_2Cl_6, boils at 184°, which is 62° higher, although it is richer in the more volatile constituent. The analogy between this example and the chlorides of iron permits us to draw a conclusion as to the molecular weight of the latter compounds. As C_2Cl_4 is more volatile than C_2Cl_6, it may be regarded as probable that Fe_2Cl_4 would be more volatile than Fe_2Cl_6. But since, in reality, ferrous chloride, which is represented by $FeCl_2$ or Fe_2Cl_4, is much more difficult to volatilise than ferric chloride, the molecule of which is shown to be Fe_2Cl_6 by Avogadro's law, it follows that the molecular weight of ferrous chloride is undoubtedly larger than Fe_2Cl_4, perhaps Fe_4Cl_8, or still larger. There is no means of ascertaining how large it is.

There are many such cases in which the molecular weight may be deduced from the volatility. The value of this method is not at present very great, as it only renders an approximate, not an exact, determination of the molecular weight possible, and it can only be applied to a comparatively small number of bodies.

§ 153. A closer investigation of the internal movements of liquids, especially friction, diffusion, and conductivity of heat, will yield the safest means of determining the weights of the molecules which actually exist in the liquid state. But the theory of these phenomena would require a special development, based on a definite idea of the properties of the molecule, before it would be possible to draw conclusions as to the values for the molecules from the observations which have been and have yet to be made.

If we attempt to form an idea as to the manner in which the internal movements of liquids depend on the weight of the molecules and on the molecular volume, calculated from the density and molecular weight, we are inclined to assume that in the movements which continuously take place in the interior of liquids, a particle will change its place more

rapidly, and penetrate between the others more easily, if its velocity is large and the volume small. But the molecular volume is proportional to the quotient of the molecular weight by the density. The velocity will generally decrease with an increased molecular weight, as is the case with gases, but probably according to a less simple law, at present unknown. According to this supposition the rate of diffusion should increase as the weight and volume of the molecules of the diffusing body decrease. But if we compare these conclusions with the results of observation, we find that the reverse frequently occurs, that bodies the chemical formulæ of which represent a larger weight and volume diffuse more rapidly than those the formulæ of which correspond to a smaller weight and volume. According to the experiments of J. H. Long[1] the quantities in column IV. (represented in terms of the molecular weights F, column II.) diffused into pure water in equal times and under similar external conditions from solutions containing in equal volumes the quantities of the salts represented by their formulæ.

I.	II. F	III. V	IV. n	V. H
Potassium iodide .	KI = 165·6	55·5	823	− 5110
„ bromide .	KBr = 118·8	45·9	811	− 5080
„ chloride .	KCl = 74·4	38·4	803	− 4440
Ammonium chloride .	NH_4Cl = 53·4	35·2	689	− 3880
Sodium iodide . .	NaI = 149·5	43·4	672	+ 1220
Ammonium bromide .	NH_4Br = 97·8	42·4	629	− 4380
Sodium chloride . .	NaCl = 58·4	26·2	600	− 1180
Lithium chloride .	LiCl = 42·4	20·9	541	—
Sodium bromide . .	NaBr = 102·8	34·2	509	− 150
Ammonium nitrate .	NH_4NO_3 = 80·0	47·2	680	− 6320
Potassium „ .	KNO_3 = 101·0	48·6	607	− 8520
Sodium „ .	$NaNO_3$ = 84·9	38·4	524	− 5060
Lithium „ .	$LiNO_3$ = 68·9	28·9	512	—

A comparison of columns III. and IV. shows that for bodies of analogous composition, the higher rate of diffusion generally corresponds to the larger value of the volume, V. More than 800 particles of potassium iodide and only 600

[1] 'On the Diffusion of Liquids,' Inaug. Dissertation, Tübingen, 1879; *Wied. Ann.* ix. 619.

particles of sodium chloride diffuse in the same space of time, although the volume of a particle of the latter is scarcely half the size of a molecule of the former. Either the theoretical views previously stated are incorrect, or the formulæ used do not represent the actual molecular weights, or both are incorrect. But it is evident that tolerably simple and definite relations do exist between the rate of diffusion and the composition of bodies. Potassium and ammonium compounds diffuse more rapidly than the corresponding sodium compounds, and these more rapidly than lithium. In compounds of the same metal the iodide diffuses more rapidly than the bromide, the bromide more rapidly than the chloride, and the chloride than the nitrate; sodium bromide forms an exception.[1]

Long has pointed out that, almost without exception, the more rapidly diffusing bodies use up a larger quantity of heat on solution than those which diffuse less rapidly. This disappearance of heat, as heat of solution (column V., under H), may be due to two causes. It is either used in overcoming the cohesive force of the dissolved body, consequently in overcoming molecular attractions, or else it is used in producing certain molecular motions which are not heat and which are peculiar to the liquid but not to the solid state, or finally the heat is partly expended for each purpose. At any rate it is rendered latent by resolving the continuity of the solid body, by converting the solid mass into a liquid. The bodies are not necessarily split up into particles represented by the formulæ in column II. under F; the decomposition may extend further in some cases than in others. The larger values for the heat of solution indicate a more complete decomposition, *e.g.*, if potassium chloride is split up into particles of the composition n (KCl), and sodium chloride into m (NaCl), m is probably larger than n. It is probable that none of these salts really separate into the molecules represented by the formulæ, as the acids almost without exception diffuse incomparably more rapidly than the salts which are formed from them by neutralisation. This fact is most easily explained

[1] This exception is not due to an error of observation, since Graham observed that NaBr diffuses more slowly than NaCl. He found that 590 NaBr 696 KI, and 600 NaCl diffuse in the same time.

on the supposition that several molecules of the salt have united to form a single molecule.

§ 154. The slower diffusion of the salts is in many cases due to another kind of increase in their molecular weight or volume, viz. to their union with a certain quantity of water, which is generally, but not always, identical with their water of crystallisation. Numerous observations on solution, solubility, supersaturated solutions, the colour and the vapour tension of solutions,[1] and particularly Rüdorff's [2] investigations on the freezing of saline solutions, have proved or made it exceedingly probable that the combination with the water of crystallisation generally survives the solid state of aggregation and still continues to exist within certain limits in the solution.

Rüdorff found that the freezing point of the solutions, *i.e.* the temperature at which they begin to deposit ice, falls in proportion to the concentration of the solutions, *i.e.* the amount of solid matter contained in them. But in many cases this regularity is only apparent when a certain quantity of water in addition to the given salt is taken into consideration. This quantity of water is generally, but not always, the same as that with which the salt crystallises at the particular temperature.

Rüdorff's results have been confirmed to a great extent by de Coppet,[3] who repeated a portion of the experiments and extended the investigation. The observations of the two physicists for the same series of salts yield somewhat different results as to the amount of water of crystallisation present. This contradiction can only be explained by more careful determination of the temperature. Guthrie [4] has also made experiments in this direction.

In the following table the first column contains the name of the dissolved substance; the second, under Q, the amount of substance expressed by its formula producing the depression of the freezing point; the third, under *t*, the depression of the

[1] Wüllner, *Pogg. Ann.* 1858, ciii. 529, cv. 85; 1860, cx. 387.

[2] *Pogg. Ann.* 1861, cxiv. 63; 1862, cxvi. 55; 1872, cxlv. 599.

[3] *Ann. Chim. Phys.* [4], 1871, xxiii. 366; 1872, xxv. 502, xxvi. 98; [5] 1875, vi. 275. The first paper contains a historical survey of former observations on this subject.

[4] *Phil. Mag.* [4], 1876, i. 354, ii. 211.

freezing point (expressed in degrees centigrade) produced by one part by weight of the substance dissolved in 1,000 parts by weight of water; the fourth, under tQ, the depression which the freezing point suffers when the quantity Q, represented by the molecular formula, is dissolved in 1,000 parts of water. The numbers in column IV. show how many degrees the freezing point of a solution of the quantity Q in 1,000 parts of water lies below the freezing point of water. Rd signifies Rüdorff, and Cp, de Coppet.

	Q	t		tQ	
		Rd	Cp	Rd	Cp
Potassium chloride .	KCl = 74·4	0·0446	0·0451	3·32	3·36
„ bromide .	KBr = 118·8	0·0292	—	3·47	—
„ iodide .	KI = 165·6	0·0212	—	3·51	—
Ammonium chloride .	NH_4Cl = 53·4	0·0653	0·0660	3·48	3·51
Potassium sulphate .	K_2SO_4 = 173·9	0·0201	0·0224	3·50	3·90
„ chromate .	K_2CrO_4 = 194·3	0·0194	0·0196	3·77	3·81

For other substances the freezing point of the solution falls more rapidly than is required by the diminution in the amount of anhydrous substance contained in it, because a part of the water remains combined as water of crystallisation, and the remainder only acts as a solvent. The freezing point falls in proportion to the amount of hydrated salts in the solution.

	Q	t		tQ	
		Rd	Cp	Rd	Cp
Magnesium sulphate	$MgSO_4 . 7\,H_2O$ = 245·5	0·0072	0·0073	1·77	1·79
Zinc „	$ZnSO_4 . 7\,H_2O$ = 286·4	0·0058	0·0055	1·66	1·58
Nickel „	$NiSO_4 . 7\,H_2O$ = 280·1	0·0055	—	1·54	—
Ferrous [1] „	$FeSO_4 . 7\,H_2O$ = 277·4	—	0·0055	—	1·53
Copper „	$CuSO_4 . 5\,H_2O$ = 248·9	0·0065	0·0070	1·62	1·74

[1] Observed by Blagden.

The two observers have obtained different results in the case of certain salts, acids, and alkalies. Rüdorff concludes that sodium chloride is anhydrous at temperatures below $-9°$, but that it exists in solution as $NaCl2H_2O$, below this temperature. De Coppet assumes that the solution of sodium chloride contains one or more hydrates at higher temperatures.

According to Rüdorff sodium bromide and iodide are combined with $4H_2O$; according to de Coppet they are united to $3\,H_2O$. Even if the uncertainty of the observations is not taken into account, it is not at present possible to decide whether the quantities under Q are identical with the molecular weights. But the relations pointed out by Rüdorff make it clear that if the molecular weight m is not equal to the quantity Q, it must be a simple multiple of it.

Therefore $\mathfrak{M} = n \,.\, Q$ where $n = 1, 2, 3, 4 \ldots$ or any whole number.

Since equivalent quantities of analogous compounds depress the freezing point to approximately the same extent, it may be assumed that in such a group of compounds n has one and the same value.

It must be remembered that all these numbers apply only to temperatures below the freezing point of water. It has long been known that the quantity of water combined with the different substances frequently changes with change in temperature. This has been largely confirmed by Rüdorff's investigations.

The concentration of the solution also influences the amount of combined water. Cupric chloride contains three times as much combined water in the dilute blue solution as it does in the concentrated green solution. The former contains $CuCl_2\ 12\ H_2O$, and the latter $CuCl_2\ 4\ H_2O$. According to Rüdorff the amount of combined water also changes below the freezing point in a solution containing from 16 to 20 per cent. of anhydrous cupric chloride. The change of colour on warming shows that, at higher temperatures, even dilute solutions contain the green, lower hydrated salt.

§ 155. The heat which is absorbed on dissolving a solid does not, as a rule, disappear immediately on the change to the liquid state, but a considerable portion of it is absorbed

only when the concentrated solution which is formed is diluted by a further addition of the solvent. It may be concluded from this peculiar phenomenon that the quantities under Q in the table in the above paragraph are not under all circumstances identical with the molecular weights which hold good for the liquid state. On the contrary, the molecular weights are greater than these quantities. This gradual disappearance of heat can only be explained on the supposition that the larger groups of molecules preserve their coherence on solution, but on a greater dilution of the solution they are split up by the action of the solvent, thus causing a further absorption of heat. For example, a concentrated solution of potassium nitrate suffers a diminution in temperature, on dilution. It is, therefore, very improbable that when this body is dissolved, it at once splits up into single molecules of the composition KNO_3. It is probable that this only occurs in very dilute solutions, perhaps only in warm solutions, or it may be that the simple molecule is never formed.

It may be assumed with a tolerable amount of certainty that the quantity $Q = KNO_3 = 100{\cdot}9$ is only a fraction of the molecular weight of this substance. We can now understand the fact observed but not explained by Rüdorff and de Coppet, that in the case of many substances the freezing point sinks more slowly than the concentration of the solution increases, as for instance in the case of the nitrates of potassium, sodium, ammonium, silver and lead.

When larger aggregations of molecules form, as the concentration is increased and the temperature falls, a certain quantity of salt will lower the freezing point to a smaller extent than it would in a more dilute solution freezing at a higher temperature, because the freezing point falls, as has been shown by numerous examples, in proportion to the number of molecules present. Four parts by weight of silver nitrate dissolved in 100 parts of water lower the freezing point from 0° to − 0·7°. But if the 100 parts of water already contain 40 parts of silver nitrate, a further addition of four parts only lowers the temperature from − 4·85° to − 5·10°, = 0·25°. The molecular aggregations in the 40 per cent. solution appear to be almost three times the size of those in the dilute solution.

In many cases it is necessary to assume the existence of larger groups of molecules—to explain, for instance, the softening of bodies before melting. The peculiar condition of certain organic tissues and similar substances, produced by the imbibition of liquids, representing possibly a state of matter midway between the liquid and the solid, may be explained on this assumption. The difficulty with which substances, called colloids by Graham,[1] diffuse through porous membranes, may also arise from the fact that they are composed of larger aggregations of molecules.

Although these different methods for determining the molecular weight in the liquid state are at present imperfect and uncertain, they permit us to hope that it will be possible in the future to determine the relative if not the absolute weight of the molecules. To accomplish this many investigations made for this special purpose are required.

§ 156. The determination of the molecular weight of solid bodies appears to be even more difficult than in the case of liquids. Up to the present the only guide to this determination which has proved of any service is isomorphism. The possibility of arriving at the value of the molecular weight by means of isomorphism depends on the supposition, that isomorphous replacement is produced by the same number of molecules, therefore the quantities which replace each other without producing any alteration in the crystalline form of the compound, stand in the same ratio to each other as do the molecular weights. The accuracy of this assumption has not yet been proved; it nevertheless possesses a great degree of probability. But the conclusions arrived at by the aid of isomorphism are of only a slight importance, as the isomorphous groups do not represent many compounds, and secondly, the molecular weight of not even a single compound is known with such a degree of certainty that it could be used as a standard of comparison for the rest.

The only conclusion which can be arrived at with certainty is, that the molecular weight of many, perhaps very many substances, must be considered to be greater than the quantity represented by their empirical formulæ.

[1] *Phil. Trans.* 1861, 183. *Ann. Chem. Pharm.* 1862, cxxi. 1.

The empirical formula for titanic acid is TiO_2. But anatase, one form of this trimorphous substance, is isomorphous with scheelite $CaWO_4$, scheelitine $PbWO_4$, and wulfenite $PbMoO_4$. Anatase must therefore contain four atoms of oxygen and have the formula Ti_2O_4, since the quantity represented by this formula can replace the compounds indicated by the above formulæ without producing any change in crystalline form. Fergusonite, which consists essentially of niobate of yttrium, is isomorphous with these four compounds. Hence the formula will probably be $YNbO_4$.

Although many similar cases are known, all the deductions from isomorphism as to the value of the molecular weight remain isolated, for the reasons previously mentioned. Our survey of this subject can only be aided by a comprehensive comparison of the crystalline form and composition of numerous compounds. Even then it will scarcely be possible to ascertain the actual molecular weights, but we shall learn that certain values which are now frequently regarded as molecular weights are only fractions of actual molecules. Certain numbers will be excluded as too small, but there will be no guarantee that those stochiometric quantities which are large enough to satisfy all the conditions of the law of isomorphism are not smaller than the true molecular weights.

These and similar observations show how difficult it is to ascertain the size of the molecules in solids and liquids. It is possible that the progress of science may yield further means for solving the problem. Some of the physical properties of bodies may provide the desired aid. It is also possible that in many cases the notion of molecules in the strict sense no longer corresponds to the existing circumstances and that a distinct isolation of these systems of matter from each other does not occur. In any case great caution is required in applying views deduced from gaseous bodies to liquids and solids.

§ 157. Ignorance of the molecular weights of liquid and solid bodies does not prevent the determination of their atomic linking, though it renders the solution of the problem much more difficult. All previous observations show that we may assume with a tolerable amount of certainty that, in

passing from the gaseous to the liquid or solid states of aggregation, the order of the atoms in the chain is rarely changed. In the rare cases where a change occurs it is, as a rule, detected by the changed properties of the substance. Consequently it appears to be permissible to assume that substances have the same atomic linking in the liquid and solid state as they have in the gaseous state. We are all the more entitled to make this assumption, as our views on atomic linking have to a certain extent been derived from and confirmed by the behaviour of solid, and especially of liquid compounds. We have even gone a step further by assuming that when new elements or radicals are substituted for elements or radicals of similar valency, contained in a compound, the order of the remaining atoms is not, as a rule, disturbed. Our views on the atomic linking of those salts whose molecular weight and constitution have not been directly determined, whilst those of the acids from which they are derived are known, depend on this supposition. The atomic linking of many acids, which do not volatilise without decomposition, has been deduced from the constitution of their ethers or ethereal salts, by means of the same hypothesis. This deduction is in this case made in a manner similar to that described in § 148; the determination of the molecular weight of a compound being made by comparison with compounds of known molecular weights. The atoms or radicals which replace the hydrogen of the acids are supposed to occupy the position of the replaced hydrogen.

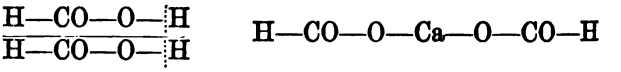
When the new atoms or radicals are like hydrogen monovalent the case is very simple; the hydrogen is replaced by the new elements atom for atom; *e.g.*

Hydrochloric acid HCl	yields	Potassium chloride KCl
Formic acid H—CO—O—H	yields	Potassium formate H—CO—O—K
Acetic acid H_3C—CO—O—H	yields	Methyl acetate H_3C—CO—O—CH_3

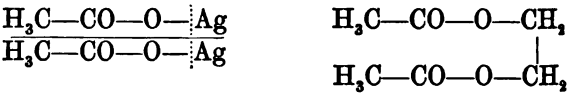
When polyvalent atoms or radicals replace the monovalent

hydrogen they satisfy the affinities which formerly attached the hydrogen. Here, again, the matter is quite simple so long as only one atom of hydrogen is replaced in each molecule, *e.g.*

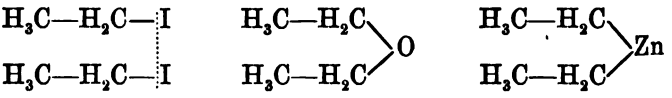
Two molecules of formic acid yield one molecule of calcium formate:



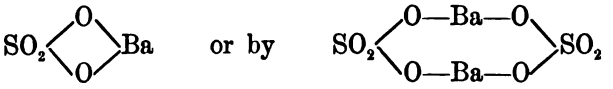
and two molecules of silver acetate yield one molecule of ethylene acetate:



These changes are analogous to the double decompositions which have been proved by Avogadro's law to take place when 2 mols. of ethyl iodide are converted into 1 mol. ethyl ether or 1 mol. zinc ethyl:



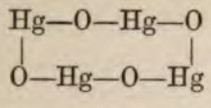
It has already been pointed out in § 148 that a degree of uncertainty exists when two or more atoms of hydrogen in the same molecule are replaced. Thus it is doubtful whether the constitution of barium sulphate is represented by



or by a larger closed chain.

The same uncertainty exists with regard to the oxides of unknown molecular weight, as has been already pointed out in § 150. The formulæ, which have been arbitrarily chosen on account of their simplicity to indicate the molecular weights of the oxides of zinc and mercury, ZnO and HgO, can hardly represent the constitution of these oxides correctly. Small molecules like these would certainly be very easily volatilised, as both their constituents are volatile. It is much

more probable that the molecules of these oxides form long closed chains, such as



&c.[1]

These and numerous other cases of the uncertainty in our knowledge of the atomic linking of liquid and solid bodies are chiefly due to our ignorance of the molecular weights which these bodies really possess. The progress of the science in this direction is entirely dependent on the discovery of a good method by which it will be possible to ascertain the molecular weights in the liquid and solid state, as logically and consistently, and with the same degree of uniformity and thoroughness, as can be done for the gaseous state by the aid of Avogadro's hypothesis.

[1] This view has been expressed recently by L. Henry. (*Etudes de chimie moléculaire*, Brussels, 1879, extract from the *Annales de la Société scientifique de Bruxelles*, 1879.)

IX.

THE CHEMICAL VALUE, VALENCY, OR CAPACITY OF SATURATION OF THE ATOMS.

§ 158. One of the most important suppositions upon which the present doctrine of atomic linking depends, and also that of the constitution or structure of chemical compounds which has grown out of this doctrine, is the knowledge of the chemical value of the atoms, which has been variously styled valency, capacity of saturation, or is denoted by the number of bonds of affinity which an atom possesses. The doctrine of valency is, as already mentioned in §§ 90–93, a recent development of the theory of chemical types, which at first were simply empirical. The observation that the power of elements to combine with others differs not only in the intensity with which this combination takes place, but also in the number of atoms with which an atom of a given element can combine, showed the necessity for the introduction of a doctrine such as that of valency. Further, the doctrine of 'chemical equivalents,' although used for some time, but never consistently, has by this means been fully developed, and a clear explanation been given of its relation to the doctrine of atomic weights, with which it had been hitherto only too frequently confounded. The valency of an atom is represented by the proportion of its atomic to its equivalent weight; it is, therefore, a whole number. This number represents the number of times that equivalent weight of an element is contained in its atomic weight.

The laws by which the atomic weights of the elements are determined have already been fully described. There therefore remains to be mentioned what the present interpretation of the idea of equivalent weights is, an interpretation which has varied considerably in the course of the development

the chemical atomic theory. It is well known that the expression 'equivalent' was proposed by Wollaston, with the intention of replacing Dalton's entirely hypothetical atomic weights by a number determined empirically. Wollaston himself was not, however, consistent in carrying out the idea of equivalency as expressed by the word equivalent. His so-called equivalent weights[1] were, to a great extent, atomic and molecular weights, and in reality as hypothetical as those of Dalton, differing only in being determined from another point of view.[2] The same remark applies to the equivalent weights used by Gmelin and other later authorities.

The cause of this is to be found in the nature of the subject itself, for no weights of any two elementary bodies are completely equivalent, but are at the most approximately so, as regards one or more points. Hence very different equivalent weights have been proposed, according to the different views adopted in regarding this approximate equivalency. The doctrine of electrolytic equivalency, which regards as equivalent those quantities separated electrolytically by one and the same electrical current in a given time, is capable of a more consistent application than any other doctrine of equivalency. Nevertheless, this view has not been thoroughly and consistently carried out, for in the case of a large number of elements, multiples of the electrolytic equivalents have been used, *e.g.* the equivalents accepted for nitrogen, phosphorus, arsenic, and antimony are three times their electrolytic equivalents. In some cases these electrical equivalents have been regarded and used as atomic weights; they are distinguished from the 'simple atoms' of Berzelius and the atomic weights at present in use, since they are determined by the aid of Faraday's law of electrolysis, and not by the hypotheses of Avogadro and of Dulong and Petit.

The necessity for a complete distinction between equivalent and atomic weights, in order that the two ideas may be used

[1] *Vide* Kopp, *Gesch. d. Chem.* ii. 375.

[2] Dalton's atomic weight of N was identical with its present equivalent weight, whilst Wollaston's so-called equivalent weight was identical with its present atomic weight. According to Dalton the formula for ammonia was NH, whilst according to Wollaston it was NH_3.

side by side, but not in place of one another, was first recognised during the strife between the dualistic and the unitary or typical chemical theories. By the recognition of this distinction the idea of chemical equivalent has become simpler and more definite; in fact, it has become so limited in meaning as to represent equality in one respect only. At the present time those quantities of different elements are regarded as equivalent which combine with the same number of single atoms of one or more elements; and thus the intensity of the force with which these atoms are held together is entirely disregarded, and also the properties of the compounds produced by this union.

Experience has shown that hydrogen has the smallest atomic weight of all elements, and also the smallest equivalent weight; also that the atomic weight of every other element is equivalent, at least, to the atomic weight of hydrogen, often to some multiple of it, but never to a fraction of it. Hence the atomic weight of hydrogen is taken as the unit for equivalent weights, and therefore the equivalent weight of an element is that quantity of an element which is equivalent to one atom of hydrogen.[1]

By the acceptance of this unit the numerical expressions of valency are reduced to the greatest possible simplicity. As far as we can judge from our present knowledge, the valency of all elements may be expressed by one of the whole numbers from 1 to 6, or probably from 1 to 8. The atomic weight of any element is equivalent to either one or two or three atoms of hydrogen; or an element may be either mono-, di-, trivalent &c., *i.e.* the atom of this element can combine with as many atoms as may be combined with 1, 2, 3, 4, 5, 6, 7, 8 atoms of hydrogen.

§ 159. One of the most important, but at the same time one of the most difficult problems which Chemistry has to solve at the present time, is the determination of the equivalent, or what amounts to the same thing, the valency of an element. Before the means for the solution of this question can be con-

[1] This hypothesis has not, however, remained unquestioned. Geuther (*Zeitsch.* [2], vi., 1 Suppl. 119) believes that hydrogen may, under certain circumstances, be tri- or pentavalent.

sidered, it will be necessary first to discuss the preliminary question which has in recent times been frequently raised in a variety of forms, viz. as to whether valency is a constant *magnitude*, an invariable property of the atoms, or whether it represents only an intrinsic property of the atoms dependent upon and variable with external circumstances. This question has never been discussed with the clearness to be desired; nevertheless the extent of the conclusions, which will be different according as to whether a negative or affirmative reply has been arrived at, has always been correctly estimated.

Since the aim of all scientific investigations is to exhibit the most variable phenomena as dependent upon certain active invariable factors taking part in them and in such a manner that each phenomenon appears to be the necessary result of the properties and reciprocal action of these factors; then it is clear, that chemical investigation would be considerably advanced were it possible to prove that the composition of chemical compounds is essentially determined by the valency of the atoms and the external conditions under which these atoms react upon one another. The first necessary step in this direction has been made in the attempt to explain the regularities observed in the composition of chemical compounds, by the assumption of a constant power of saturation or an invariable valency of the atom. The opposite and equally hypothetical assumption that the valency is variable, leads to no advancement. The first step towards progress in this matter would be made, if some hypothesis as to the cause of this variability were proposed. This difference between the two attitudes has seldom been properly realised. Whilst some chemists, accepting the constant valency of atoms, have attempted to deduce the varying atomic linking from one distinct point of view, others have considered it sufficient to have assigned to the atom of a particular element in one compound one valency, and in another compound a different valency, according as this or that value appeared the most suitable, and thus to have given a so-called explanation of the composition of the compounds in question. In this way the fact has been overlooked, that an arbitrary interpretation carried out by means of chosen hypotheses, cannot be regarded as an attempt

at a scientific explanation, but is nothing more than an expression of our ignorance of the causal connection of the phenomena. An explanation would require that the different valencies assigned to one and the same element in different compounds, should be traced to a distinct cause.

If, for instance, it is stated that carbon in carbon dioxide possesses double the valency which it possesses in carbon monoxide, such a statement is no explanation of the fact that an atom of carbon in the former compound is combined with twice as much oxygen as in the latter, for such a statement is merely a paraphrase, which hides its incompetency by assuming the form of an explanation. Although this may be perceived without further remark, still it has frequently occurred during the last few years that similar paraphrases have not only been proposed but also accepted as real explanations of such phenomena. Just as it was formerly supposed, that the assumption of a vital force dispensed with a more complete investigation of the phenomena of animal life, so many chemists have of late thought that they possessed in 'variable valency,' a means of explaining the varying stochiometric relationships which would satisfy all claims. Such deceptions can only retard the advance of the science, since they prevent an earnest and thorough investigation of the question, whether each atom is endowed with a property determining and limiting the number of atoms with which it can combine, dependent upon the intrinsic nature of the atom and like it invariable; or whether this ability is variable and with it the nature of the atom itself.

It is by no means impossible that the magnitudes, which we now style atoms, may be variable in their nature. The variability of the atoms themselves is no longer so improbable, especially since the variation in the specific heat, one of the fundamental properties of the atoms, has been recognised. Since the dependency of the specific heat upon temperature can be explained by the change of the conditions of motion of invariable atoms; and the atoms, so far as our experience goes, have hitherto shown themselves to be throughout constant and invariable in many important respects, it is advisable to regard the atoms for the present, and until the

contrary is proved, as invariable magnitudes. It is also advisable to attempt to show that the varying composition of chemical compounds is dependent upon an invariable valency of the atoms and the varying conditions under which it makes itself felt, or by which its action is influenced to a greater or less extent. Should such an attempt be unsuccessful, then in order to found a theory agreeing with facts, the changes which may be supposed to take place in the atoms themselves must be ascertained, and the causes of these investigated.

§ 160. In the determination of the equivalent weight and of the valency of an element, certain conditions must be fulfilled, which, as the conception of equivalency was less definite, were formerly regarded as superfluous and unnecessary. Those quantities of the elements were regarded as equivalent, which combined with the same quantity of another element, with a total disregard as to whether or not the elements in the compound formed exercised an equal number of combining units. But consequent to the development of the theory of atomic linking, the idea of equivalence has been so fixed in this respect, that only those quantities of different elements are regarded as truly equivalent, which possess the same number of combining units, *i.e.* those quantities which are able to combine with the same amount of other substances directly and without the intervention of a third substance. Hence it is necessary to ascertain the mode of atomic linking in those compounds, from the composition of which the valency of an element is to be deduced.

The limitation introduced into these definitions, that the elements must be directly united together in the compound and not indirectly combined by means of other elements, forms the most essential distinction between the views formerly held on this subject and those of the present time. This limitation has, however, considerably increased the difficulties of determining the equivalent weight of an element, but this was necessary in order to give definiteness to the problem, and to render possible the attainment of an unequivocal solution of the question. The introduction of more definite ideas served to overcome the influence of a pernicious caprice, which had for a long time rendered the idea of chemical equivalence of very

doubtful import, making equivalent weights variable magnitudes and completely hiding and confusing their relations to atomic weights.

Whilst formerly the knowledge of the composition of one or more compounds of an element was thought sufficient to determine the equivalent weight of that element, we now require a knowledge of the atom-linking in these compounds, and this requires that the molecular weight of the compound and the atomic weight of the element concerned should also be known. It will, therefore, be easily understood that the equivalent weight cannot, as was formerly supposed, be determined alone from a knowledge of the stochiometric composition of any particular compound. Moreover, all those compounds are unsuited for such determinations in which the atomic linking is not known with accuracy and exactness sufficient to allow of a definite statement, as to which particular atoms each atom of the element, the equivalent of which is to be determined, is directly combined. Those compounds afford the most accurate means of determining the equivalent of an element which contain in their molecule a single atom of the element united to monovalent atoms or radicals; since thereby the possibility of a combination of the atoms amongst themselves is excluded, and consequently all must be regarded as united directly with the single atom of that element, whose equivalent weight is required. The compounds contained in the table in § 90 may be cited as typical of what is required, as also may those compounds corresponding to them containing monovalent hydrocarbon radicals, such as methyl iodide, IMe_1, ethyl iodide, IEt_1, methyl fluoride, FMe_1, mercuric ethide, $HgEt_2$, boric ethide, BEt_3, silicon ethide, $SiEt_4$, &c. Besides the compounds already cited in the above table, the following are specially important for the determination of the valency, viz. methyl fluoride, MeF_1, zinc methide, $ZnMe_2$, and lead methide, $PbMe_4$; from the molecular weight and composition of these compounds it is seen that fluorine can combine with one, zinc with two, and lead with four monovalent radicals.

§ 161. If the attempt be made to determine the valency of the elements from the composition of the above compounds

and those given in § 90, it will be perceived at once that some elements form compounds containing different quantities of monovalent elements, *e.g.* HgCl and $HgCl_2$, PCl_3 and PF_5, WCl_3 and WCl_6. The question then arises, whether mercury is monovalent in mercurous chloride, and divalent in mercuric chloride; similarly whether phosphorus is tri- and pentavalent, and tungsten penta- and hexavalent. This question would not have been so much discussed if an understanding as to the meaning of valency had been previously arrived at. If the expression mono-, di-, and trivalent, is simply to indicate the number of monovalent atoms, or their equivalent, with which an element is united, then, of course, mercury is monovalent in calomel (HgCl) and divalent in corrosive sublimate ($HgCl_2$). These descriptions are nothing more than an expression of the stochiometric composition of the compounds, and as such are not unfrequently used, owing to the want of more convenient expressions.

If, on the other hand, the valency be defined as a property of the atoms, expressing their ability to unite with a certain number of other atoms, then the question arises as to whether or not this ability is variable. According to the one view the atom changes its own nature, according to the number of the atoms with which it is united; thus monovalent mercury differs from divalent mercury, in possessing one combining unit less; in the same way tri- and pentavalent phosphorus differ from one another. According to the other view, the atom itself remains unchanged, whether it be united to a greater or lesser number of atoms of another element. Just as the power of a magnet is not estimated by any particular weight which it may happen to carry, but only by the maximum weight it can support, similarly the capacity of saturation of an atom is not determined by the number of other atoms with which it is combined in any particular compound, but only by the greatest number with which it is possible for it to combine. According to this conception mercury in calomel combines with one atom of chlorine not because its nature has changed, but because it cannot combine with more than is offered to it.

This view is without doubt the simpler. It is, at least,

superfluous to suppose that the capacity of saturation, or valency, varies with the degree of saturation.[1] From the fact that the higher compounds may be prepared from the lower ones, it cannot be doubted that the valency or the capacity of saturation is not exhausted in the lower compounds, and hence these latter do not afford a means of determining the valency.

§ 162. The possibility of the combining units in many compounds being unsaturated has been denied, and many attempts have been made, although without sufficient reason, to avoid altogether the acceptance of unsaturated affinities in compounds.

Although it is probable in many organic compounds which were formerly supposed to contain free combining units that some of the carbon atoms are united by two affinities, *e.g.* in the olefine series of hydrocarbons, C_nH_{2n}, yet there are many other compounds to which such or similar explanations cannot be applied.

The carbon atom in carbon monoxide is apparently saturated by the oxygen atom to half its capacity only. To explain this by the statement that the two remaining affinities are united with each other, a view accepted by some chemists, is, so far as our present knowledge is concerned, only another way of describing the fact. The existence of two free combining units explains the ease with which carbon monoxide unites with chlorine to form phosgene gas.

$$O{=}C{=}^{\cdot\cdot} + Cl{-}Cl = O{=}C{=}Cl_2.$$

The fact that this combination takes place only in sunlight, might be cited in support of the view that the combining units are not free, but are first rendered so by the action of light. This argument is, however, but feeble, since the necessity for the action of light is completely explained, inasmuch as it is required to loosen or dissolve the union existing between the two chlorine atoms united to form the molecule.

[1] Many misunderstandings have arisen from the confusion of the ideas of 'saturation' and power of saturation, expressions frequently used as synonymous with valency. Examples of this may be seen in the work by Geo. A. Smyth, *On the Development of the Theoretical Views on the Conjugated Sulphur Compounds*, Berlin, 1876, ix. 4.

It is also easy to understand how it is that the free combining units of carbon monoxide are not saturated by free oxygen at the ordinary temperature, but require a higher temperature; since, in order that combination may take place, the molecule of oxygen must first be dissociated,

$$2CO + O.O = 2CO_2,$$

this combination therefore takes place more easily at higher than at lower temperatures. E. Ludwig[1] has shown that it takes place also at lower temperatures in presence of the loosely combined oxygen of chromic acid.

Carbon monoxide unites with many other substances to form compounds in a manner similar to that in which its combination with chlorine and oxygen is effected. Cuprous chloride, for example, combines with chlorine, oxygen, and also carbon monoxide. It is still more remarkable that carbon monoxide can expel many metals from their compounds, *e.g.* it expels zinc and sodium from the compounds of these metals with ethyl (C_2H_5), the ethyl groups uniting with carbon monoxide to form diethyl ketone, $C_2H_5.CO.C_2H_5$.[2]

Nitric oxide (NO) is undoubtedly an unsaturated compound, as is also nitric peroxide, NO_2, at temperatures above 150°. These compounds are unsaturated whether we regard nitrogen as tri- or pentavalent, and in both cases the number of free combining units is an uneven one. Hence the subterfuge, that the affinities of one and the same atom are able to combine with one another, used to explain away the free combining units in carbon monoxide, cannot avail in such cases.

The ease with which nitric oxide is oxidised by oxygen at the ordinary temperature, is generally recognised as the important condition upon which the manufacture of sulphuric acid depends. Just as it combines with oxygen, so does nitric oxide combine directly with chlorine, bromine, and other substances.

§ 163. It has been shown that some metals form unsaturated compounds. Thus according to Mitscherlich the

[1] *Ann. Chem. Pharm.* 1872, clxii. 47.

[2] J. A. Wanklyn, *Phil. Mag.* [4], 1866, xxxi. 505.

vapour densities of mercurous chloride and bromide are 8·35 and 10·14 respectively, and therefore these compounds have the following molecular weights:—

235·3 HgCl and 279·7 HgBr.

It appears, therefore, that in the molecule of these compounds only one combining unit of the divalent atom of mercury is saturated. In order to avoid this irregularity Kekulé[1] assumes that, in the solid state, these compounds have molecular weights corresponding to the formula Hg_2Cl_2 and Hg_2Br_2 respectively, and that in the passage to the gaseous state they decompose into the metal and the higher chloride and bromide as follows:—

$$Hg_2Cl_2 = Hg + HgCl_2$$
$$Hg_2Br_2 = Hg + HgBr_2.$$

The mixture produced in accordance with this view would have the same mean vapour density as that of the compounds the molecular weights of which are expressed by the formulæ HgCl and HgBr. This view, therefore, is not in contradiction with the observed facts. In further support of this the fact may be cited that corrosive sublimate (mercuric chloride) is always formed, although in small quantities only, when calomel (mercurous chloride) is sublimed.[2] At the same time it is not to be overlooked that these assumptions of Kekulé do not remove the difficulty; for instead of two molecules HgCl, each containing one free combining unit, we obtain a completely saturated molecule $HgCl_2$ and an atom of mercury, which has two combining units unsaturated. Nor is it clear why the one atom of mercury should take away the chlorine atoms from another and exactly similar atom, instead of the chlorine atoms remaining equally divided between the two atoms of mercury. If, on the other hand, we acknowledge the correctness of the other view, viz., that mercurous chloride in the gaseous state exists as HgCl, then it is still permissible to suppose that in the passage of the gas into the solid state two

[1] *Lehrbuch*, I. 498.

[2] Gmelin, *Handb.* 5 Aufl. iii. 511; confirmed later on by Erlenmeyer and Odling (*v.* Will's *Jahresbericht*, 1864, 280).

molecules unite with one another by the free combining units to form a saturated molecule, Hg_2Cl_2.

If other compounds containing partially unsaturated combining units are to be regarded in an analogous manner, then to be consistent we must regard carbon monoxide as a mixture of carbon dioxide and free carbon, and nitric oxide as consisting of free nitrogen and oxygen, thus:—

$$2\overset{\text{iv.}}{C}\overset{\text{ii.}}{O} = \overset{\text{iv.}}{C}\overset{\text{ii.}}{O_2} + \overset{\text{iv.}}{C}$$

$$2\overset{\text{iii.}}{N}\overset{\text{ii.}}{O} = \overset{\text{iii.}}{N}\overset{\text{iii.}}{N} + \overset{\text{ii.}}{O}\overset{\text{ii.}}{O}.$$

Suppositions, the futility of which is evident.

But, if we suppose that two of the combining units of tetravalent carbon in carbon monoxide are unsaturated, and in nitric oxide one of the tri- or pentavalent nitrogen, then there is no difficulty in supposing that in the molecule of mercury (and also of cadmium) two unsaturated combining units exist, and one in each of the molecules of mercurous chloride and bromide. This is all the more evident when it is remembered that the affinities of mercury are weaker than those of nitrogen or carbon.

The atoms of the above-mentioned metals can scarcely be supposed to be the only ones which can exist in the unsaturated, or only partially saturated condition. Observations on the dissociation of chemical compounds would lead us to conclude that all chemical compounds would, at sufficiently high temperatures, be resolved into atoms. Should this be the case, then at these temperatures the atoms of all elements must exist in an unsaturated state. It cannot, therefore, appear strange that this should be the condition of things for some elements at comparatively low temperatures.

If, therefore, it be recognised that the existence of unsaturated or partially saturated atoms and molecules is not to be denied, then we must guard against attempts being made to determine the valency of elements from unsaturated compounds. Otherwise the results obtained would be too low.

The danger of such an error does not at first sight appear to be great, inasmuch as unsaturated compounds are easily recognised by the ease with which, by combining with other

atoms, they are converted into saturated ones; and therefore the discovery of the existence of free combining units cannot be difficult.

§ 164. In the meantime it must not be forgotten that the saturation of free combining units is dependent upon several conditions, not always apparent. The mere existence of unsaturated combining units in atoms in contact with one another, does not necessarily suffice to bring about a combination. Whether combination does or does not take place, depends more upon the intensity of the attraction which the unsaturated atoms exert towards each other, and this again upon the chemical nature of the two atoms;[1] and further, upon the external conditions under which they are brought in contact—more especially is this true with regard to temperature. Supposing the attraction which the two unsaturated atoms A and B exert upon each other is less than that exerted by A on C, then it may happen that the compound A C is formed under conditions of temperature, &c., which do not permit of the formation of A B. Hence it would be erroneous to conclude that A does not contain unsaturated combining units because it does not unite with the unsaturated atom B. If the powers of attraction which A possesses are in general weak, then it may happen that it can only combine with a few, or perhaps only one other element. Nor can it be definitely stated that the elements chosen in such experiments are the right ones, or that the conditions under which the experiments are made are the ones required. From a theoretic point of view it does not appear at all impossible that an atom or a radical may possess affinities, and consequently exercise attraction on others, but these are so feeble that saturation of them under the conditions of our experiment is impossible. If such an extreme case were to occur, then it would probably escape our observation, and is therefore not of special interest. The possible conception of such a case, however, enables us to recognise the inequality in value possessed by the positive and negative results of experiments made with the object of determining the valency of the

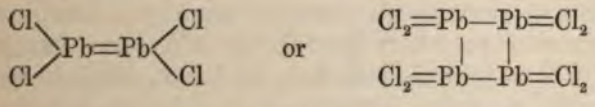
[1] This was pointed out by E. Erlenmeyer in 1864. (*Zeitschrift Chem. u. Pharm.* vii. 629.)

lements. Whilst the production of a single compound is vidence of the existence of combining units, yet a hundred ruitless attempts to prepare a compound can never be regarded as showing conclusively the absence of affinities.

§ 165. In the case of the majority of the elements, there are no compounds the molecular weights of which can be determined, and, therefore, in many cases the valency of the elements must be deduced from the stochiometric composition of those compounds containing the element combined with monovalent atoms only. In such cases the valency is represented by the greatest number of monovalent atoms with which an atom of the element in question unites to form a compound.

In such cases also, the valency may be found to be too small, for the compound investigated may contain several atoms of the element in question, united with one another.

For example, from the composition of its highest chloride, lead would appear to be divalent, whereas from the molecular weight of the methyl compound $Pb(CH_3)_4$, it follows that lead is, in reality, tetravalent. This apparent contradiction is very easily explained by the supposition that lead chloride contains several atoms of the metal united to one another by two combining units, thus:—



From this example it is clear how, from our ignorance of he molecular weight of compounds, we may easily assign too mall a value to the valency of an element.

Such cases are not infrequent, and the ability of the atoms f the elements to combine with one another may be suitably escribed as self-saturation.

Iron affords another instance of this same phenomenon f self-saturation, in its highest chloride, which contains three toms of chlorine combined with one atom of iron. Since it as been found that the molecular weight of this compound is epresented by the formula Fe_2Cl_6 (§ 23), then iron must be more than trivalent in this compound. For if each atom of iron is united by three combining units to three atoms of

chlorine, then there must at least be one combining unit required to hold the atoms of iron together. Whether these atoms are held together by more than one combining unit, that is to say, whether iron is more than tetravalent, cannot be decided from the above. A similar statement holds good of aluminium, the molecular weight of the chloride of which has been found to be Al_2Cl_6.[1]

It appears, then, from these examples, that in those cases where the molecular weight of suitable compounds is not known, the valency of an element of known atomic weight may, when calculated from the stochiometric composition of its compounds, be found too small, but, as a rule, not too great.

In order to avoid the errors arising from the ignorance of the molecular weight, in all cases where it has been possible, such compounds have been used to determine the valency of an element, the density of which in the gaseous state could be determined. This precaution is at any rate justifiable in all cases where, as in the case of lead, the valency of the element deduced from the compound of known molecular weight, is greater or not less than that calculated from other compounds.

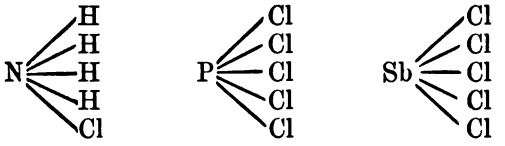
§ 166. But it has often happened that those compounds which volatilise without decomposition have been used in preference to those which are decomposed by volatilisation, even in such cases where the valency as deduced from them is smaller than that deduced from the latter. Kekulé notably has rejected all those compounds of nitrogen, phosphorus, arsenic, and antimony which in the solid or liquid state contain five monovalent atoms combined with one atom of these elements, but which in the conversion into the gaseous state are resolved into two atoms of the monovalent element and compounds containing three atoms of the monovalent element united to one atom of the elements, nitrogen, &c. In similar way, in determining the valency of sulphur and its allied elements, this chemist has rejected all those compounds containing more than two monovalent atoms.

The views adopted by Kekulé possess two great advantages, first, according to these views the valency of the

[1] From other properties of this element, which will be described later on, it would appear that its atom is only trivalent.

elements is only deduced from compounds of known molecular weight, and consequently the law of atomic linking is not applied to those compounds, from the composition of which it cannot be deduced; secondly, all those compounds in which the elements appear to possess a higher valency than in any of their gaseous compounds, are brought together under one common head, a position which, at least in many cases, without doubt is perfectly justifiable. Later observations have shown, however, that Kekulé had extended his views too far by applying them to compounds which are now regarded as undoubtedly containing the atoms linked by single combining units.

Whilst, for instance, the existence of well-characterised compounds, such as ammonium chloride (NH_4Cl), phosphonium bromide and iodide (PH_4Br, PH_4I), phosphorus pentachloride and pentabromide (PCl_5, PBr_5), antimony pentachloride ($SbCl_5$), and others containing five monovalent atoms combined with one element of the atom in question, led Gerhardt[1] and Couper[2] to regard nitrogen and analogous elements as pentavalent in a series of compounds; Kekulé,[3] on the other hand, holds that in those compounds decomposed on volatilising, the combination is not produced by the same kind of forces as those holding the atoms together in the molecules of gaseous compounds, but is due to the attraction exerted by the atoms of the closed molecule NH_3 on those of the molecule HCl, or of the atoms in the molecule of PCl_3 on those of the molecule Cl_2 and so on. In other words Kekulé does not regard these compounds with five monovalent atoms as correctly represented by the formulæ:—

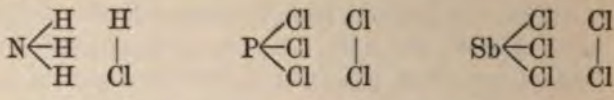


[1] *Traité de Chimie Organique*, iv. 608, note.

[2] *Ann. Chim. phys.* [3] 1858, 53, p. 488.

[3] In various places in his *Lehrb. der organ. Chemie*, e.g. pp. 142, 143, 145. A synopsis of these views will be found in the reply to Naquet, *Compt. rend.* 1864. lviii. 510.

but as due to the juxtaposition of two molecules in the following manner—



These compounds are, therefore, considered as analogous to double salts, to the compounds of salts and other substances with water of crystallisation, in short with a large number of compounds which chemists have from the earliest times regarded as formed by the union of several closed molecules.

Kekulé consequently has styled compounds of this kind as 'molecular,' in contradistinction to the 'atomic' compounds. These views have found many supporters.

The contention between these opposing views was at first especially complicated, inasmuch as many of the supporters of the views of Couper disputed the alleged decomposition of the compounds in question in their conversion into the gaseous state. Although the occurrence of this decomposition has been undoubtedly proved, still on the other hand observations have been made [1] proving that under certain conditions some of the compounds with five monovalent atoms, more especially PCl_5 and PF_5, can exist in the gaseous state, and, therefore, there are no reasons for denying a pentavalency to the atom of phosphorus contained in them.

Accordingly, if the compounds of phosphorus with five monovalent atoms, although partially decomposed by the conversion into vapour, give the correct valency of the phosphorus atom, the same will probably be found to be true of the closely allied elements nitrogen and arsenic, although the pentavalent compounds of these elements in conversion into vapour decompose into trivalent compounds.

These and similar examples show that in determining the valency of an element, all non-volatile compounds should not be disregarded, as otherwise the valency of the elements would often be found too low.

Although for a large series of compounds the views of

[1] *Vide* §§ 31 and 90.

Kekulé cannot at present be altogether dispensed with, yet, on the other hand, there is a danger of attributing too high a value to the valency of elements, from the study of non-gaseous molecular addition compounds.

§ 167. Various explanations may be given of the fact that an atom holds certain atoms more strongly than others of the same kind. It is possible that the atoms of these elements possess stronger and weaker affinities, of which only the former are in the position to attract other atoms contained in gaseous molecules. But it is also possible that all the affinities possess the same power, but that owing to the saturation of some of them, the intensity of the others is thereby weakened to such a degree, that they can no longer form compounds. Finally, it is also conceivable that the affinities are all equally powerful, but that the positions or directions in which they tend to hold the atoms of other elements, are owing to the motion of the molecule submitted in varying extent to the influence of the centrifugal force and other forces and motions opposed to the holding together of the atoms, so that the atoms are propelled from some of these positions or along certain lines, and on the other hand are held fast in other positions and directions.

Each of these three modes of explanation appears to be permissible.

The question as to whether the affinities of one and the same atom, and consequently the forces of attraction with which it tends to combine with these atoms, are completely equivalent, or whether they differ in intensity and perhaps in quality also, is one which is by no means so easily answered as might, at first sight, be supposed.

First of all it has not, as has already been pointed out in § 108, been shown whether what we style the affinities or combining units of an atom, are in reality individual and distinct forces, tending to bring the atoms upon which they act into certain relations in space relative to the atom attracting them. If a horse-shoe magnet can carry a load of four pounds, then we are not justified in representing it as possessing four individual forces of attraction each amounting to one pound. But we can imagine a combination of two

magnets laid across one another, of which each of the four poles can carry one pound but no more. We are still not in a position to say whether the forces of attraction of a tetravalent atom resemble the former magnetic action more than the latter. Assuming there are as many single forces as the combining units exhibited by the atom, then from the observation that a polyvalent atom, *e.g.* P, gives up more easily than others certain of the atoms with which it can unite, *e.g.* Cl_2 from PCl_5, we cannot conclude at once that combining units are unequal. For the saturation of some of the equally strong forces of attraction may suffice to change the power of the remaining ones, the atoms already combined may be in the way of others; further, the increase in molecular weight produced by the addition of new atoms will change the motion of the molecule and perhaps, in consequence, its coherence; the single atoms may also be differently affected by the rapid motion of the molecule, especially by the centrifugal force, and consequently their separation will be more or less facilitated.

On the contrary it has always been rightly supposed, that the difference of the combining units of an atom would be proved or rendered probable, if two isomeric, not identical compounds, could be prepared containing an atom of a given element combined with several atoms of another element, so that the difference of properties could only be due to the different mode of combination of identical atoms. It was formerly supposed that some isomerides of this character were known, *e.g.* two compounds having the composition CH_3Cl were thought to exist, and hence the difference in the combining units of one and the same carbon atom was regarded as demonstrated. When, however, it was recognised that the observations from which the existence of these isomerides had been concluded were based on error, and that the substances regarded as isomeric were moreover identical, then the acceptance of such differences in the combining units appeared superfluous and was almost universally abandoned. The possibility of the existence of such was nevertheless repeatedly assumed, although many of the experiments made with the view of

adducing experimental proof yielded but negative results.[1] Even at the present day such isomerides are sought amongst the numerous compounds containing one single polyvalent atom combined directly with all the other atoms. We only know one of each of the compounds having the following composition, CH_3Cl, CH_2Cl_2, $CHCl_3$, CH_3Br, &c. In the case of other elements isomerism of this character has hitherto been unobserved. Supposing the atom of phosphorus to possess three strong and two weaker combining powers, then each of the compounds $POCl_3$, $POBr_3$, $PSCl_3$, $PSBr_3$, &c. might be expected to exist in three isomeric forms, according as the oxygen or sulphur atom is attached by two strong, two weaker, or one strong and one weak combining unit. Hitherto nothing of the kind has been observed.

In the past few years, however, besides some few observations which have excited considerable opposition, others of unquestionable accuracy have been made, showing that under some conditions a polyvalent element may combine with monovalent radicals (*i.e.* atomic groups) in such a manner as to produce several compounds of identical composition, which are not identical but only isomeric with one another. Such observations have been made in the case of the elements sulphur and nitrogen.

§ 168. In continuing a series of investigations first suggested by Kolbe, Krüger observed that the compound of ethyl sulphide with methyl iodide differs from the compound produced by the combination of ethyl methyl sulphide with ethyl iodide; and consequently there are two isomeric compounds, the composition of which is expressed by the formula

$$\begin{array}{l} \quad\quad\quad\

differences Krüger concluded that the four combining units of the atom of sulphur are not identical.

Some thirty years after A. W. Hofmann[1] had experimentally investigated the question as to whether it was possible to distinguish which of the hydrogen atoms in ammonia was eliminated and replaced by a radical. W. Lossen made the remarkable observation that in hydroxylamine, NOH$_3$, (a compound discovered by Lossen) by the substitution of three hydrogen atoms by two kinds of acid radicals R′ and R″, a large number of isomeric compounds are produced, whereas according to the knowledge hitherto attained as regards the mode of combination of the atoms, only one such compound could be predicted Lossen found that by the introduction of one radical twice and the other once, from six to nine isomeric compounds were produced, differing from one another in their crystalline form, melting-point, solubility, and other properties. These compounds are resolved into three different groups, the production of which is determined by the order in which the radicals are substituted in the molecule. This is represented in the following table, in which the position of R represents the order in which the radical indicated by it has been introduced:—

I.	NHHHO	+ R′Cl	= NR′HHO	+ HCl
	NR′HHO	+ R′Cl	= NR′R′HO	+ HCl
	NR′R′AgO	+ R″Cl	= NR′R′R″O	+ AgCl
II.	NR′HHO	+ R″Cl	= NR′R″HO	+ HCl
	NR′R″AgO	+ R′Cl	= NR′R″R′O	+ AgCl
III.	NHHHO	+ R″Cl	= NR″HHO	+ HCl
	NR″HHO	+ R′Cl	= NR″R′HO	+ HCl
	NR″R′AgO	+ R′Cl	= NR″R′R′O	+ AgCl

The products of the three modes of preparation, viz.:

I.	II.	III.
NR′R′R″O	NR′R″R′O	NR″R′R′O

differ not only in their physical properties, but also exhibit very distinct differences in their chemical behaviour. For

[1] *Annalen*, 1850, lxxiv. 158.

example, when treated with aqueous hydrochloric acid the radical which was the last to be introduced is the first to be eliminated, as follows:—

$$NR'R''R'O + HOH = NR'R''HO + R'OH$$
$$NR'R'R''O + HOH = NR'R'HO + R''OH$$

The nature of the radical which is removed is of influence only so far as it serves to increase or lessen the ease of the decomposition. For example, the compound is more easily and quickly decomposed when the 'anisyl' group, $An = -CO.C_6H_4.OCH_3$, is in the third place than when this position is occupied by the 'benzoyl' group, $Bz = -CO-C_6H_5$. Alkalis remove the radical introduced at the second stage first, and if this radical is 'benzoyl,' then it alone is removed, *e.g.*—

$$NBzBzAnO + KHO = NBzHAnO + KOBz.$$
$$NAnBzAnO + KHO = NAnHAnO + KOBz.$$

If the 'anisyl' group occupy the second, and benzoyl the third position, then the former is removed in smaller quantity, and the latter in larger quantities.

Chief reaction
$$NBzAnBzO + KHO = NBzAnHO + KOBz$$
$$NAnAnBzO + KHO = NAnBzHO + KOBz$$

Subordinate
$$NBzAnBzO + KHO = NBzHBzO + KOAn$$
$$NAnAnBzO + KHO = NAnHBzO + KOAn$$

If, however, benzoyl occupies the first position alone, then it retains its place—

$$NBzAnAnO + KHO = NBzHAnO + KOAn.$$

The compounds produced by these reactions—viz., the substitution of H for the radical occupying the second position, which are represented by the formula NR'HR''O—are not isomeric but identical with those formed by two stages of substitution, and represented in the foregoing passage by the formula NR'R''HO; thus, for example, $NBzHAnO$ is identical with $NBzAnHO$.

The astonishing multiplicity of the substitution products of hydroxylamine is greatly increased by the observation that

each of the compounds of the types NR'R''O, NR'R''O, and NR'R''O have been found to exist in two or three isomeric forms, which Lossen has distinguished as the α, β, and γ modifications. These differ more especially in their physical properties and to some extent in their chemical behaviour, namely, in their greater or less resistance to chemical reagents. Isomerism of this character has been observed even when all the three hydrogen atoms are replaced by one and the same radical; thus there are three different tribenzoyl hydroxylamines $NBzBzBzO$, which are also distinguished as α, β, and γ modifications.

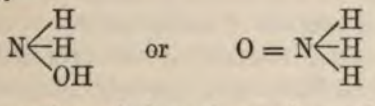
§ 169. The observations described in the last section have led to a reiteration of the view which has been abandoned by the majority of chemists, namely, that the affinities of polyvalent elements differ from one another. This view at all events appears to be the most simple explanation of these remarkable observations; its acceptance does not, however, by any means finally settle the question.

First of all, it must be remarked that hitherto not a single instance is known in which single atoms and not radicals are combined in several ways by other atoms, but, so far as our knowledge extends it would appear that the replacement of radicals by single atoms suffices to destroy the isomerism. In order to explain this fact, we must suppose that in simple compounds only one single position of the atom is stable, and that in the production of such compounds the atom continues to alter its place until it has attained this position. There is but little probability in favour of such movements since these so-called 'changes of place' occur but seldom at the ordinary temperature, and only at high temperatures do they occur with greater frequency.

But in order to explain the identity of NR'HR''O and NR'R''HO, mentioned in § 168, we must suppose even in the case of radicals that this change of position takes place very easily, since the last radical introduced must take up the position of the second immediately after its removal. Our knowledge of the alterations in atomic linkings does not, however, accord very well with such a supposition.

It must not be forgotten that the acceptance of a difference

in the combining capacities of an atom would lead us to expect in some cases a larger, and in other cases a smaller, number of isomerides than found by actual observation. For instance, we may take either of the following formulæ for hydroxylamine:—



and still the formation of three isomeric products formed by substituting R′, R′ and R″ for H appears possible.

These may, as Lossen supposed, be the compounds denoted in foregoing sections with the signs I. II. and III.

The explanation fails in the case of the three modifications α, β, γ which are also known when the radicals R are identical; it may still be supposed that the oxygen atom changes its position. Accepting this not altogether inconceivable supposition, then from the first of the above formulæ nine isomerides would be expected having the composition NR′R′R″O, and from the second thirty: but just as in the case of the three modifications, so also with the ten hydroxylamines, the non-existence of which can again only be explained as arising from an immediate inter-molecular change.

To the α, β, γ modifications one might apply the frequently used expedient, and style them 'physical isomerides,' placing them in a position parallel to the numerous cases known under various names as 'allotropic modifications,' 'polymorphous conditions,' that is to say, they would be regarded as forms of aggregation, the differences of which arise not from the mode of combination of the atoms, but are supposed to be produced by the different modes of juxtaposition of molecules identical with one another. But on the one hand these modifications do not possess the character of true physical isomerides:[1] as a rule they cannot be converted into one another, and when the conversion is possible it can only be accomplished with difficulty. Further these isomerides exhibit no inconsiderable differences in their chemical behaviour. On the other hand, it is not easily perceived why one should introduce a

[1] O. Lehmann, 'Ueber physikalische Isomerie.' Inaug. Diss. Strassburg, 1876. Zeitschrift, 1877, 97.

new hypothesis, which predicts the existence of more isomerides than we know, when we hesitate to use it consistently in explaining other instances known to us.

As the matter stands at present, it remains at any rate doubtful whether or not the supposition does not suffice that the combining capacities of the atoms are equal, and that the cause of the above-mentioned isomerism is rather to be sought in the radicals combined with the polyvalent atom than in the forces which hold them in combination. If we accept changes in the atomic linking of the atoms forming the radicals, then the hypothesis suffices to explain the special case of hydroxylamine. Lossen[1] has already pointed this out, but at the same time truly remarked that the use of such a special hypothesis is of but little value. But we are in a position to form a conception, which may be applied to all hitherto observed cases of isomerism, and which will meet the present views of molecular physics.

When a polyvalent atom combines with several monovalent atoms then each of the latter will occupy a fixed position of equilibrium relative to the former. If one of the monovalent atoms be replaced by a polyvalent one, which is itself a constituent of a radical, then this polyvalent atom will strive to occupy the place of the atom it replaces, and at the same time will take with it the other atoms, which are also constituents of the radical. If a second and third radical are introduced, the same phenomena are repeated, so far as the atoms already introduced do not close up or narrow the space. It may possibly arise that the atom by means of which the combination is brought about cannot thoroughly attain the position to which the combining capacity strives to bring it, and hence it will be less strongly combined. If the motion of the atoms and also that of the entire molecule are taken into consideration, then the hypotheses and conceptions at present in use suffice to explain why one of two radicals for which the force of attraction is identical is more easily removed than the other.

It is avowedly more simple to suppose the combining capacities, as the attractions of the atoms are styled, to be different. In preferring this view it must not be forgotten that but little

[1] *Op. cit.* 186, 49.

advance is gained; for this hypothesis is little more than a restatement of the fact that one radical, for example, is more feebly combined than another. The commencement of a real knowledge will be first attained when we have learnt to recognise the single combining capacities and to distinguish their action from that of others. We should therefore have a repetition in a new but more difficult form of the problem of orientation, which in the case of the aromatic compounds has been already brought to a considerable state of perfection.

§ 170. Before attempting to determine the capacity of saturation or valency of all known elements, it is first of all necessary to answer the question whether the valency of an element may vary with regard to different elements, or whether the same number of combining units exists in all cases.

If the stochiometrical composition of different compounds found empirically be alone regarded, then one might be inclined to regard this difference as requiring no further proof, for the number of combining capacities of different elements, which appear in their combinations with a certain fixed atom to be saturated by it, is very variable. But remembering the views propounded in § 164, that the production and the stability of compounds is not alone dependent upon the presence of combining powers, but is also influenced by the strength and intensity of these, and in such a manner that when their intensity is feeble under specially favourable circumstances only may an element possibly form a compound corresponding to its valency. The differences observed in the composition of single compounds should not immediately be attributed to changes in the valency, but an attempt should be made to find in each case whether the limit of combining power of any particular element with another is not in reality due to the low intensity rather than to the entire absence of other combining capacities. It is at present impossible to decide this question absolutely, yet it may be decided with a considerable degree of probability.

Further, since elements which resemble one another do as a rule form compounds having analogous composition, and are to be distinguished from one another only in cases where their combining capacities for the particular element are at

all feeble, then we may with tolerable certainty attribute such deviations to feeble intensity in the combining capacities.

The numerous analogies exhibited by the compounds which the elements form with fluorine, chlorine, bromine, and iodine, lead to the conclusion that each element possesses the same valency towards each one of these haloïd elements; and further, that when in case of one particular element, for example, the iodine compound corresponding to the highest chlorine compound of an element is wanting, this want may be attributed to the more feeble affinity of this element towards iodine, in consequence of which it is unable to retain in combination, under the conditions at which the highest chloride exists (*e.g.* PCl_5 and Fe_2Cl_6) a number of atoms of iodine equal in number to those of chlorine.

If from the non-existence of phosphorus penta-iodide we should draw the conclusion that phosphorus has another nature as regards iodine, in fact that it is a trivalent element, then since the stability of the compounds PF_5, PCl_5, PBr_5 gradually decreases from the fluoride to the bromide, so in order to express oneself quite accurately we ought to say that in PF_5 the phosphorus is completely pentavalent, but in PCl_5 it is beginning to become trivalent, and in PBr_5 its trivalent nature is more in the ascendency, until finally in PI_5 it is entirely trivalent.

It is well known that the oxides and sulphides of the majority of elements correspond to their haloïd compounds, containing for every two atoms of fluorine, chlorine, &c., one atom of oxygen or sulphur, and the hydroxides and sulphydrates one 'OH' and 'SH' group for every chlorine atom. There are elements the oxides of which contain more oxygen, sulphur, &c., than corresponds to the composition of their highest chlorides. For example, the highest chloride of sulphur, selenium, and tellurium contains four atoms of chlorine, whilst from the composition of their oxides and hydroxides we should expect the highest chlorides to contain six atoms of chlorine. The tetrachlorides are easily resolved into lower chlorides and free chlorine, in the case of sulphur tetrachloride (SCl_4) this change takes place at temperatures below the freezing point, and further, the trioxides

give off the third atom of oxygen with comparative ease, and the corresponding hydroxides are not volatile without decomposition; such facts indicate that the non-existence of hexachlorides may be attributed to the feebleness and not the absence of the fifth and sixth combining unit. This is all the more probable inasmuch as the element tungsten, which resembles these elements in the composition of its highest oxide, forms a hexachloride which easily loses one atom of chlorine, whilst molybdenum and chromium, elements more nearly related to sulphur, can combine with not more than five and three atoms of chlorine respectively.

From analogy it would appear probable that in the seventh group the non-existence of the chlorides, &c. corresponding to the highest oxides and hydroxides (periodic acid, &c.) arises from the feebleness of the affinity of the halogens for each other, but even these elements form compounds in which they act as polyvalent to each other.

§ 171. The matter is totally different when those compounds are considered, which the strongly negative elements of the chlorine and sulphur groups form with positive elements, with hydrogen, or the metals. Amongst the many hundred such compounds there is not a single one to be found which would necessitate that chlorine, bromine, and iodine should be regarded otherwise than monovalent, and sulphur, selenium, and tellurium than divalent.

These relations must, therefore, lead to the conclusion that chlorine, bromine, and iodine act as monovalent elements with regard to the more electropositive elements, such as hydrogen and the metals, but are polyvalent, and probably heptavalent with regard to negative elements such as oxygen; similarly that sulphur, selenium, and tellurium are divalent towards more positive elements, and hexavalent with regard to oxygen. Fluorine and oxygen would in all probability exhibit similar properties if it were possible to combine them with elements still more positive than they themselves.

The nitrogen and phosphorus group similarly show a different behaviour toward more positive elements. These elements are essentially trivalent as regards hydrogen and the metals. Ammonia, NH_3, and phosphorus hydride, PH_3, can

certainly combine with a fourth atom of hydrogen; but only when this is already attached to a strongly negative element, such as chlorine or iodine. As regards oxygen all the elements of this group are apparently pentavalent, and some of them as regards chlorine also.

Carbon and the elements associated with it are on the other hand usually tetravalent, whether they are combined with other strongly positive elements, or with negative elements, such as oxygen, chlorine, &c.

In the case of the metals there are at present no reasons for supposing such a difference in their behaviour toward more positive or more negative elements. It is, however, worthy of remark that the few hydrides of the metals which are known have not, as a rule, a composition analogous to that of the chlorides.

§ 172. The conclusion drawn from analogous behaviour of the elements would still leave room for considerable doubt, were it not for the fact that, like most of the properties of the atoms, the valency or capacity of saturation of the atoms is a periodic function of the atomic weight. The valency in the series of the natural families of the elements changes regularly from each to the next following family. Since the corresponding members of these families follow one another in the series of atomic weights, then it follows that in this series also the valency changes regularly from member to member. Starting from the maximum of atomic volume we have the following example of this regularity;—

Monovalent	Divalent	Trivalent	Tetravalent	(Towards Positive Elements)		
				Trivalent	Divalent	Monovalent
Li LiCl	Be $BeCl_2$	B BCl_3	C CH_4	N NH_3	O OH_2	F FH

This same regularity is repeated in the compounds of those elements which follow fluorine:—

Monovalent	Divalent	Trivalent	Tetravalent	(Towards Positive Elements)		
				Trivalent	Divalent	Monovalent
Na NaCl	Mg $MgCl_2$	Al $AlCl_3$	Si SiH_4	P PH_3	S SH_2	Cl ClH

It is worthy of notice that the valency of lithium, sodium, beryllium, and magnesium accepted in the above is that deduced from the quantitative composition of their compounds of unknown molecular weight. Consequently it is probable that the valency so accepted, *i.e.* the apparent valency, is identical with the real. But it is noticeable that in order to retain the same regularity in the second series as that exhibited in the first, the apparent valency of aluminium must be used, and its atom must be considered as trivalent, whilst the molecular weights of its volatile compounds, Al_2Cl_6, Al_2Br_6, Al_2I_6 (*vide* § 114) show that it must, at least, be tetravalent.

Regularities of a similar character are found when, instead of the compounds with the positive element hydrogen, those with the negative element chlorine are considered. Thus for the elements comprising the sixth horizontal series in the table in § 61 we have the following :—

$AgCl$	$CdCl_2$	$InCl_3$	$SnCl_4$	$SbCl_3$ $SbCl_5$	$TeCl_2$ $TeCl_4$	ICl ICl_3

Those chlorides in the upper line in this table may be volatilised without decomposition, whilst those in the lower line are decomposed when converted into vapour.

§ 173. The greatest regularity, as was first pointed out by Mendelejeff,[1] is to be found in the composition of the oxides, which, with few exceptions, changes in a regular manner with increase in atomic weight. As a general rule it is found in the arrangement of the elements according to their atomic weights that the amount of oxygen combined with an atom of another element increases by half an atom from member to member of the series, but this increase never goes beyond four atoms, when it sinks again to half an atom. This relationship is best exhibited when, in order to avoid fractions of atoms, the stoichiometric composition of the oxides, without regard to the molecular weight, is so expressed that the formulæ used give the number of atoms of oxygen combined with two atoms of the element in question. This is illustrated in the following table, which also contains some oxides enclosed in brackets; these are not known with certainty, or not in a

[1] *Annalen*, 1871, Suppl. Band viii. 133.

state of purity, but from the analogies to nearly related compounds, there can be but little doubt of their existence.

OXIDES.

(Li_2O)	Na_2O	K_2O	Cu_2O	(Rb_2O)	Ag_2O	Cs_2O	—	Au_2O
Be_2O_2	Mg_2O_2	Ca_2O_2	Zn_2O_2	Sr_2O_2	Cd_2O_2	Ba_2O_2	Ng_2O_2	Hg_2O_2
B_2O_3	Al_2O_3	Se_2O_3	Ga_2O_3	Y_2O_3	In_2O_3	Ce_2O_3	Yb_2O_3	Tl_2O_3
C_2O_4	Si_2O_4	Ti_2O_4	—	Zr_2O_4	Sn_2O_4	—	—	Pb_2O_4
N_2O_5	P_2O_5	V_2O_5	As_2O_5	Nb_2O_5	Sb_2O_5	—	Ta_2O_5	Bi_2O_5
O_2O_4[1]	S_2O_6	Cr_2O_6	(Se_2O_6)	Mo_2O_6	Te_2O_6	—	W_2O_6	—
F ?	(Cl_2O_7)	Mn_2O_7	(Br_2O_7)	—	(I_2O_7)	—	—	—
—	—	(Fe_2O_6)[2]	—	Ru_2O_8	—	—	Os_2O_8	—
—	—	Co_2O_3[3]	—	Rh_2O_4	—	—	Ir_2O_4	—
—	—	Ni_2O_3	—	Pd_2O_4	—	—	Pt_2O_4	—

The oxides in the above table are, in the majority of cases, those which are known to be the richest in oxygen; many of the metals in the first horizontal series form oxides containing still more oxygen, thus, for example, Na, K, Cu, Ag, Au, and probably Li, Rb, and Cs. These oxides are, as a rule (as are also many introduced into the above table), peroxides, which easily lose a portion of their oxygen; copper oxide, CuO, or Cu_2O_2 alone is very stable. Some of the elements in the second series also form peroxides, *e.g.* Ca_2O_4, Sr_2O_4, Ba_2O_4. In the third series only one element of the earth metals has, for the sake of simplicity, been introduced. Inasmuch as cerium forms an oxide CeO_2 or Ce_2O_4, so we could replace Ce_2O_3 by La_2O_3, and write Ce_2O_4 in the fourth series without disturbing the regularity. Deviations occur in this table only in the case of the following elements: O, F, Fe, Co, Ni, Rh, Pd, Ir, and Pt. These probably arise from the fact that the affinity of these elements for oxygen is not sufficiently strong to form a compound containing a quantity of oxygen corre-

[1] Ozone, the molecular weight of which is probably O_3.

[2] The anhydride of ferric acid is probably FeO_3 or Fe_2O_6 (*vide* Gmelin's *Handbuch der Chemie*, 5 Aufl. iii. 244; 6 Aufl. 382). Mendelejeff (*op. cit.* 147) has proposed the formula FeO_4 or Fe_2O_8 for it, but has not advanced any proof in support of this view.

[3] Mendelejeff (*loc. cit.* 147) accepts the formulæ CoO_2 or Co_2O_4 for the oxides of cobalt, and appears to regard the latter as the anhydride of the so-called cobaltic acid. The composition of this substance has, however, been found to be Co_2O_3 (*vide* Liebig and Kopp, *Jahresber.* 1856, 398); the existence of the oxide CoO_2 is doubtful.

sponding to its valency. This is all the more probable as those oxides of these elements containing the greater amount of oxygen, contain a portion of it but loosely held, and consequently part with it easily.

It cannot well be doubted that the composition also of oxides not introduced into the table is dependent in a more or less simple manner upon the atomic weights of the elements. In many series this is easily seen; for instance, in the case of the lower oxides of tin and those metals nearly associated with it, we have the following regularity :—

$$Sn_2O_2,\ Sb_2O_3,\ Te_2O_4,\ I_2O_5.$$

A similar regularity may be exhibited in other series. But the experimental investigation of all the oxides of known elements is not sufficiently advanced to allow of a complete review of all possible oxides, and consequently to discover the general law regulating their composition. In the case of many elements the preparation of different oxides has scarcely been attempted.

§ 174. It has been known for some time that the composition of the oxides stands in a very near relationship to that of other compounds, *e.g.* with that of the hydroxides and salts. Mendelejeff has, however, demonstrated this in a manner which exhibits with remarkable clearness the law which this relationship obeys. The composition of the hydroxides or hydroxyl compounds, whether they are of a basic or acid nature, is, on the one hand, dependent upon that of the oxides, and, on the other hand, upon that of the hydrides or hydrogen compounds. In general, each atom of oxygen, as a divalent element, may be replaced by two monovalent atoms or radicals, *e.g.* by two monovalent hydroxyl groups, OH. But in the majority of cases it appears that not more than four such groups can combine with an atom of a polyvalent element. In the few cases where more than four hydroxyl groups are combined with an element, they are, as a rule, held but feebly, somewhat after the manner of the water in halihydrates ;[1] the hydrogen contained in them exhibits neither basic nor acid properties, and hence is not easily replaced by the

[1] *Vide* § 179.

atoms of metals or acid radicals. The number of hydroxyl groups having sharply defined characters which can enter into combination is determined in a remarkable manner by the composition of the corresponding hydrogen compounds; hydrides and hydroxides contain the same number of hydrogen atoms. Instead of hydrides, the compounds with monovalent hydrocarbon radicals, *e.g.* those with ethyl, C_2H_5 or Et, which are often more easily prepared, may be used as indicators, since the number of these radicals is throughout equal to that of the atoms of hydrogen.

The following table exhibits the regularity just described, for the series of elements from sodium to potassium :—[1]

Oxide	Hydroxide	Hydride	Ethide
Na_2O	$NaOH$	—	$NaEt$
Mg_2O_2	$Mg(OH)_2$	—	$MgEt_2$
Al_2O_3	$Al_2(OH)_3$	—	$AlEt_3$
Si_2O_4	$Si(OH)_4$	SiH_4	$SiEt_4$
P_2O_5	$PO(OH)_3$	PH_3	PEt_3
S_2O_6	$SO_2(OH)_2$	SH_2	SEt_2
Cl_2O_7	$ClO_3(OH)$	ClH	$ClEt$
K_2O	$K(OH)$	—	KEt

The formulæ of the oxides in this table are, in order to avoid fractions, so written that they contain two atoms of the particular element. In the case of the hydroxides, hydrides, and ethides, the necessity for so writing them does not exist; the quantities expressed by their formulæ contain only one atom of the element in question, and consequently correspond to half the quantity of oxide given in the first column. Each hydroxyl, HO, in the hydroxides, replaces one-half the oxygen in the oxide.

Mendelejeff has also attempted to bring the water of crystallisation of salts under fixed rules, similar to those applied to the number of hydroxyl groups which can combine with one element. Up to the present but a short notice[2] only has been published, which serves, however, to show how far Mendelejeff has been able to pursue this subject. It can scarcely

[1] Sodium and potassium ethides are not known in the isolated state, but only in combination with zinc ethide.

[2] *Ber. d. deut. chem. Ges.* 1870, 931.

appear doubtful that these compounds are subject to law in this manner, for in the first case the combination of oxygen and hydrogen, usually regarded as water of crystallisation, must be dependent upon the nature of the atoms of these elements.[1]

§ 175. Based upon the regularities in the composition of chemical compounds described in the foregoing sections, which might be illustrated by many other similar tables, the general statement may be made that the valency of an element, as deduced from the composition of its compounds, is a periodic function of the atomic weight. The periods correspond very nearly with those of the general chemical character, and in such a manner that, as far as the element potassium, one of its periods corresponds to one of those of the atomic volume, and beyond this point to two of the periods of atomic volumes. The first three minima of the valency coincide with the first three maxima of the atomic volumes, but the first maxima of the former, C and Si, coincide with the first minima of the latter. From potassium upwards the minima of valency, Cu,[2] Rb, Ag, Cs, and Au[2] occur alternately near the minimum or maximum of the atomic volume, whilst the maxima of valency occur between a maximum and minimum of the atomic volume.

This periodicity of the valency is shown most clearly when it is deduced from the compounds with oxygen. This is one of the chief reasons for using the oxides for this purpose, although, on account of the divalency of oxygen and the possible double linkings which might arise from it, they would at first sight appear to afford but an unsuitable and doubtful means of determining the valency.

In this way, to some extent, oxygen attains the position of a standard, which was assigned to it by Lavoisier, and more especially by Berzelius, but of which it was robbed so long as valency and atomic linking were deduced from gaseous compounds only.

From the knowledge that valency is a periodic function of

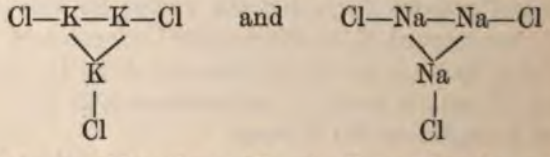
[1] Some groups of examples for the carrying out of this idea will be found in a paper by the author, *Ber. d. deut. chem. Ges.* 1872, 104.

[2] Cu and Au are regarded as monovalent.

the atomic weight, the difficulty of its determination is considerably lessened; still, many cases of a doubtful nature remain to be explained.

§ 176. Before passing on to a consideration of each of the families enumerated in § 79, it must be remarked, in the first place, that the single characteristics of valency are more distinctly shown in the periods or series, *i.e.* by those elements occupying the horizontal lines in the table in § 61, than in the groups, or those elements in the vertical lines of this table.

The group IA, containing the alkali metals Li, Na, K, Rb, and Cs, appears from what has been stated in §§ 172–174, to be constituted of monovalent elements, and has for a long time been generally regarded as such. But there is not a single compound of any member of this group the molecular weight of which is known. At any rate, the existence of an unstable polyiodide, KI_3, although generally regarded as a molecular compound, might be cited as evidence of the polyvalent nature of this group of elements. Geuther [1] concludes from the composition of the polysulphides that the alkali-metals must be either mono-, tri-, or pentavalent. A. Wanklyn [2] also expressed some years ago the opinion, which at all events has not yet been confirmed, that potassium and sodium are trivalent. In accordance with this view the chlorides would not be expressed by the formulæ K—Cl and Na—Cl, but probably by the formulæ Cl—K = K—Cl and Cl—Na = N—Cl, or



A little consideration will, at all events, show that the formulæ KCl, &c., are but little suited to the properties of the chlorides. A chloride of so volatile a metal as potassium, and having a molecular weight KCl = 39·04 + 35·37 = 74·41, would not, in all probability, be less volatile than the chlorides of mercury. The comparative non-volatility of potassium

[1] *Jen. Zeitschr.* [2] 6, 1, Suppl. 119.

[2] *Chem. Soc. Journ.* 1869, vii. p. 199; Strecker, *Jahresber. d. Chem.* 1869, 13.

chloride would be more easily understood if its molecular weight were three times the above, viz. $K_3Cl_3 = 223{\cdot}23$, and still better if it were greater.

Strictly speaking, the formulæ KCl, NaCl, AgCl, &c., have little greater value than the formula CCl for Julin's chloride of carbon, or CH for benzene had, until it was known that the molecular weights of these compounds were expressed by the formulæ C_6Cl_6 and C_6H_6, and that carbon is tetravalent in other compounds.

The matter is made still more doubtful by comparing the above with the elements forming the second section of this group, viz. Cu, Ag, and Au; for besides the chlorides CuCl, AgCl, AuCl, there are the well-defined compounds $CuCl_2$ and $AuCl_3$, and the oxides corresponding to them, from the composition of which copper appears to be divalent, and gold to be trivalent. From analogy, silver might also be regarded as polyvalent, more especially as it forms a peroxide, AgO, or Ag_2O_2, and then the monochlorides would be expressed by the following formulæ: Cl—Cu—Cu—Cl, Cl—Ag—Ag—Cl, and Cl—Au—Au—Cl. The fact that we know no compound of silver in which an atom of this metal has been demonstrated to be divalent, cannot be regarded as interfering with our acceptance of the above formulæ, for it is very possible that all compounds of silver at present known may contain two atoms of silver combined with one another, and consequently appear monovalent, *e.g.* NO_3—Ag—Ag—NO_3, &c. No compound of copper and iodine is known having the formula CuI_2, but only the one having the formula Cu_2I_2, the composition of which may be expressed most simply by the formula CuI. The isomorphism of the lower silver and copper sulphides can scarcely be understood, unless in the latter the existence of a divalent group—Cu—Cu—be accepted, and also a similar group—Ag—Ag—be supposed to exist in the former. At the same time, it must not be forgotten that these monochlorides resemble those of mercury and thallium in their insolubility in water, their change on exposure to light, and in many other characteristic properties, and that, at least in the gaseous state, these last-mentioned compounds have molecular weights corresponding to the formulæ HgCl and TlCl

(*vide* § 23). From analogy, therefore, we might regard the formulæ CuCl, AgCl, and AuCl, as representing the molecular weights of these compounds.

Nevertheless, there is one characteristic in which the whole of the first family agrees, viz. all those compounds in which these elements appear as polyvalent are converted by heat into those in which they appear as monovalent elements. Copper oxide, CuO, is, however, an exception; the sulphide, CuS, on the other hand, conforms to this rule.

§ 177. The members of the second family, consisting of the two groups A: Be. Mg, Ca, Sr, Ba, and B: Zn, Cd, Hg, are divalent in their more common and most stable compounds. The peroxides, which indicate a higher valency for these elements, are decomposed by heat. Geuther [1] regards these metals as di, tetra, hexa, octo, or deca-valent.

The last member, viz. mercury, has a tendency to act as a monovalent element. But the compounds in which it behaves as such are less stable than the normal compounds. Whilst the higher compounds of the first family are easily resolved by heat into the lower ones with a loss of negative atoms, the lower mercury compounds, on the other hand, are under different circumstances easily resolved into the metal and the corresponding higher compounds, thus:

$$2HgCl = Hg + HgCl_2, \quad 2Hg_2O = Hg + HgO.$$

In both families, therefore, the normal compounds are the more stable.

The members of the third family in the first group, of which we have B, Al, Sc, Y, La, Di, Ce, Yb, and a number of other elements which have not been thoroughly separated from one another and hence are but little known, appear to be trivalent. The elements comprising the second group also appear to be trivalent; this group contains the following easily fusible metals, Ga, In, and Tl, the oxides of which are easily reducible. Although these metals are as a rule trivalent, yet the possibility of a higher valency is not completely excluded.

The molecular weights expressed by the following formulæ, Al_2Cl_6, Al_2Br_6, and Al_2I_6 (compare § 23) require that each

[1] *Loc. cit.*

atom of aluminium should at least possess four combining units. Again cerium forms a peroxide CeO_2, and consequently this element might be placed in the first group of the fourth family. On the other hand the last member of this family, viz. Thallium, as is also the case in the second family, forms like mercury, compounds in which it appears either unsaturated or monovalent.

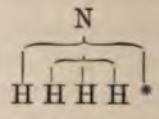
The members of the fourth family are throughout tetravalent; in the first group we have the elements C, Si, Ti, Zr, Th, and in the second group the elements Sn and Pb. Still carbon appears unsaturated in carbon monoxide, and the last member, lead, resembles mercury and thallium in its tendency to form compounds in which it appears to have a lower valency than the rest, in fact it would appear to be either unsaturated or its apparent divalency is formed by combination with itself. Under these conditions it forms compounds isomorphous with Ba, Sr, and Ca.

§ 178. In the fifth family, containing in the first group V, Nb, (Di), Ta, and in the second group N, P, As, Sb, and Bi, the difference in behaviour towards positive and negative elements is first exhibited, although not very markedly. As regards negative elements their valency is one unit greater than that of the members of the fourth family, that is to say they are pentavalent; and as regards strongly positive elements, more especially in their hydrogen compounds, they have a valency one unit less than that of the members of the fourth family, in other words they are trivalent. These facts are not exhibited in all compounds, but most distinctly in the oxides and hydrides.

N, P, As, and Sb alone combine with hydrogen to form compounds such as NH_3, PH_3, &c., and as in fact the intensity of the affinity decreases with increase in atomic weight, it cannot therefore appear remarkable that it no longer exists in the case of bismuth. Both of the first two elements, N and P, can combine with a fourth atom of a positive element when the fifth combining capacity is itself combined with a negative one (*e.g.* $NH_3 + HCl = NH_4Cl$, and in many other cases); under these circumstances, the elements are pentavalent. The constitution of the numerous salts formed by the union of

ammonia with acids can only be explained by aid of this hypothesis.

In these compounds the group of atoms NH_4, or ammonium, acts, in accordance with the theory proposed by Berzelius, as a monovalent radical, and in many cases behaves like an atom of potassium, rubidium, cæsium, &c., and in such a manner as to render confusion with the compounds of these metals possible. The radical can, however, only have one free combining unit when nitrogen is pentavalent; for only then can the four atoms of hydrogen leave one embracing unit free, thus:



The analogies exhibited by these compounds to those of the alkali metals, both in their physical properties and their chemical behaviour, as for instance in the case of ammonium chloride, NH_4Cl, and potassium chloride, KCl, and of ammonium sulphate, $(NH_4)_2SO_4$, and potassium sulphate, K_2SO_4, can only be expressed by the aid of such a hypothesis.

If nitrogen be regarded as trivalent, then these compounds can only be regarded as addition-products of ammonia and an acid, thus, NH_3+HCl and $NH_3+NH_3+H_2SO_4$, &c., from which formulæ all such analogies disappear.

The compounds of the substituted ammonias exhibit to a more marked degree than the salts and other compounds of ammonia itself properties arising from atomic linkings, and in such a manner that they cannot be justly considered as molecular addition compounds. For instance, if tetra-ethyl ammonium iodide, $N(C_2H_5)_4I$, be viewed as analogous to ammonium iodide, $NH_4I=NH_3$, HI, as a compound of triethylamine, $N(C_2H_5)_3$, and ethyl iodide, C_2H_5I, then the compound obtained from it by the action of moist silver oxide upon it, viz. tetra-ethyl ammonium hydroxide, $N(C_2H_5)_4OH$, must consistently be viewed as an addition-product of triethylamine, $N(C_2H_5)_3$, and ethyl alcohol, $(C_2H_5)OH$. That such a view cannot be held is shown by the fact that even at temperatures below the boiling point of water it is decomposed, and not

into triethylamine and alcohol, but into triethylamine, ethylene, and water,[1] thus:—

$$N(C_2H_5)_4OH = N(C_2H_5)_3 + C_2H_4 + H_2O.$$

This decomposition could scarcely take place at so low a temperature if this compound contained alcohol. Further, its entire behaviour is altogether opposed to such a view.

All these eight elements are pentavalent in their combinations with oxygen, the elements of the first group possessing a very considerable affinity for oxygen; in the second group, the affinity of phosphorus for oxygen is greater than that of nitrogen, whilst from phosphorus upwards it decreases step by step. In their combinations with the halogen elements the members of this group are pentavalent also. But it has already been repeatedly mentioned that the highest compounds of many of these elements are partially decomposed by heat, and that in some cases they are not very stable even at the ordinary temperature. It is to be observed, however, that the compounds are stable when a portion of their combining powers are saturated by less negative radicles.

For instance, arsenic trichloride cannot unite with chlorine directly, and hence arsenic appears to be trivalent in this compound. Its pentavalent nature is shown when one or two of the atoms of chlorine are replaced by hydrocarbon radicals, and the compounds are the more stable the more hydrocarbon radicals they contain. A. Michaelis[2] has found that arsenophenyl chloride, $(C_6H_5)AsCl_2$, combines with more chlorine, forming a tolerably stable liquid compound, $(C_6H_5)AsCl_4$, and A. Bæyer[3] has also found that arsenic dimethyl chloride or cacodyl chloride, $(CH_3)_2AsCl$, also unites with two atoms of chlorine, thus:—

$$As(CH_3)_2Cl + Cl_2 = As(CH_3)_2Cl_3.$$

The compound produced is unstable, and decomposes on a

[1] A. W. Hofmann, 1851, *Annalen*, lxxviii. 268.

[2] 'Ueber aromatische Arsenverbindungen,' *Ber. d. deut. chem. Ges.* 1875, viii. 1316.

[3] 'Ueber die Verbindungen des Arsens mit dem Methyle,' *Annalen*, cvii. 257.

very slight rise in temperature, forming methyl chloride and arsenic monomethyl dichloride, thus :—

$$As(CH_3)_2Cl_3 = AsCH_3Cl_2 + (CH_3)Cl.$$

Arsenic monomethyl dichloride exhibits but little affinity for chlorine, and only combines with it at very low temperatures; at $-10°$ it unites with two atoms of chlorine and forms arsenic monomethyl tetrachloride, thus :—

$$As(CH_3)Cl_2 + Cl_2 = As(CH_3)Cl_4.$$

This compound is similarly resolved into methyl chloride and arsenic chloride, at a temperature above $-10°$, but still below the freezing point, thus :—

$$As(CH_3)Cl_4 = AsCl_3 + CH_3Cl.$$

Arsenic trichloride so produced has so little affinity for chlorine that all attempts to form a higher chloride have failed. As the amount of chlorine increases relatively to the amount of carbon and hydrogen in these compounds, the force of attraction for chlorine is seen to diminish. Many other instances of a similar character are known.

Just in the same way if phosphorus be regarded as trivalent difficulties are at once introduced into the explanation of many of its compounds. For instance, if the atom of phosphorus is pentavalent, then the formation of the oxychloride, acid or anhydride from the pentachloride is a simple substitution of one atom of divalent oxygen for two atoms of chlorine or of the monovalent radicle OH for an atom of chlorine; thus the formation of the oxychloride from the pentachloride may be represented as follows :

$$\overbrace{Cl\,\overbrace{Cl\,\overbrace{Cl\,Cl\,Cl}^{P}}} + H—O—H = \overbrace{Cl\,\overbrace{Cl\,Cl}^{P}\,O} + H—Cl + H—Cl$$

As long as phosphorus is supposed to be trivalent then it must be supposed that an interchange of the atoms takes place, thus :—

$$\overbrace{Cl\,Cl\,Cl}^{P}—Cl + H—O—H = \overbrace{Cl\,Cl\,O—Cl}^{P} + H—Cl + H—Cl$$

The oxychloride is a compound which may be volatilised without decomposition; its molecular weight calculated from the determination of its vapour density has been found to be 153·0, corresponding to the formula $POCl_3$. At all events this compound must be viewed as containing the atoms united directly to the atom of phosphorus, whilst phosphorus pentachloride is supposed to be a molecular compound because it is easily resolved into PCl_3 and Cl_2, despite the numerous points of resemblance it exhibits to the oxychloride. This difficulty is made still greater, inasmuch as vanadium, the highest chloride of which, VCl_4, may be volatilised without decomposition, also forms an oxychloride, $VOCl_3$, perfectly analogous to the phosphorus compound, the constitution of which could not without inconsistency be explained by the views formerly held.

There are so many reasons for supposing these elements to be pentavalent it may be regarded as remarkable that, as already mentioned in § 174, the hydroxides and oxyacids of the members of this family contain as a maximum three and not five hydroxyl groups, and these therefore may be, according to the views described in § 113, regarded as the compounds of trivalent elements.

There are, however, compounds of some of the members of this family from the composition of which a valency greater than a pentavalency may be deduced. For instance, as from the composition of ammonium chloride, NH_4Cl, the conclusion is drawn that nitrogen is pentavalent, so from the composition of the well-defined and crystalline compound, NH_4ICl_4,[1] the conclusion might be drawn that nitrogen must be nonovalent also. The same conclusion might be drawn from the composition of the tetramethyl ammonium penta-iodide, $N(CH_3)_4I_5$, discovered by Weltzein.[2] In a similar manner phosphorus might be supposed to be heptavalent because it forms the compounds PCl_6I,[3] and PCl_3Br_4,[4] or to have even a higher valency, inasmuch as a compound PCl_3Br_8 exists,[5] although it certainly

[1] Gmelin, *Handb. d. Chem.* 5 Aufl. i. 907. [2] *Annalen*, 1854, xci. 41.
[3] Prepared by Baudrimont, v. *Jahresber.* Kopp and Will, 1862, 54.
[4] A. Michaelis, *Ber. d. deut. chem. Ges.* 1872, 411.
[5] Prinvault, *Compt. Rend.* 1872, lxxiv. 868; A. Michaelis, *loc. cit.* 414.

is very unstable. These compounds are generally supposed to be molecular compounds, resembling double salts, &c.

§ 179. In the sixth family, containing in the first group Cr, Mo, W, U,[1] and in the second group O, S, Se, Te, the difference in behaviour toward positive and negative elements is very strongly marked; but only the members of the second group form well-defined compounds with elements more positive than themselves. The composition of the numerous compounds with hydrogen, the metals, the semi-metals, and with other elements save some of those formed with the negative elements of this group itself and with those elements of the second group of the seventh family, may be most easily explained upon the supposition that oxygen, sulphur, &c., are divalent elements.

The elements of this family are hexavalent in their compounds with the halogen elements and with those of the oxygen and sulphur group. Nevertheless, only one of these elements is known to form a volatile compound containing six atoms of a monovalent element; this compound is tungsten hexachloride, WCl_6, which is easily resolved into the pentachloride WCl_5 and one atom of chlorine. The highest chlorides of molybdenum and uranium are the corresponding pentachlorides $MoCl_5$ and UCl_5, chromium only forms a trichloride, $CrCl_3$ (or perhaps Cr_2Cl_6). Sulphur, selenium, and tellurium form tetrachlorides, SCl_4, $SeCl_4$, and $TeCl_4$, the first of which decomposes below the melting point of ice. All the seven elements, on the other hand, combine with three atoms of oxygen, or sometimes with one or two atoms of oxygen, and four or two equivalents of hydroxyl, chlorine, &c. For instance the following compounds are known:—

	SO_3	—	TeO_3
	SO_2Cl_2	—	—
	$SO_2Cl(OH)$	—	—
	$SO_2(OH)_2$	$SeO_2(OH)_2$	$TeO_2(OH)_2$
CrO_3	MoO_3	WO_3	UO_3
CrO_2Cl_2	MoO_2Cl_2	WO_2Cl_2	UO_2Cl_2
—	$MoOCl_4$	$WOCl_4$	—
—	$MoO_2(OH)_2$	$WO_2(OH)_2$	$UO_2(OH)_2$

[1] When the atomic weight of uranium is taken as 240.

Many of these compounds, especially those containing chlorine, may be volatilised without decomposition; SO_3 and MoO_3, TeO_3, CrO_3, and UO_3 easily lose one atom of oxygen; WO_3 is scarcely volatile. The hydroxides, with the exception of $SO_2(OH)Cl$, are resolved by heat into the anhydride and water; selenic acid alone yields SeO_2 and O; $UO_2(OH)_2$ also loses oxygen.

In this case also, as with the members of the fifth family, the number of hydroxyl groups in the hydroxides is not greater than two, *i. e.* the number of hydrogen atoms with which the elements S, Se, and Te may combine directly; these compounds therefore may also be considered as containing mono- and divalent atoms united in the manner described in §§ 101 and 112, sulphur, selenium, and tellurium being supposed, like oxygen, to be divalent. This view would, however, make a very great distinction between compounds of analogous composition, as it would never occur to anyone to consider chromium, molybdenum, and tungsten as simply divalent.

In the explanation of the compounds of sulphur, &c. with monovalent atoms and radicals this view cannot be consistently applied. At all events it would require a considerable straining of ideas to regard SCl_4, $SeCl_4$, and $TeCl_4$ as molecular compounds; nor can this view be applied to explain the compounds formed with monovalent hydrocarbon radicals. More especially do the properties of triethyl-sulphine hydroxide $S(C_2H_5)_3OH$, discovered by v. Oeffele,[1] militate against the view that it is an addition-product of $S(C_2H_5)_2$, ethyl sulphide, and $(C_2H_5)OH$ alcohol, which, if sulphur is a divalent element, it must be supposed to be.

Instead of regarding these elements as divalent in their compounds with negative atoms, it is more probable to suppose that the affinity of these seven elements for the halogen elements varies in intensity, and is the lowest in the case of sulphur and the greatest in the case of tungsten, and hence it is only with this latter element that the hexavalency makes its appearance.

At the same time this consideration leads to the conclusion that the valency of these elements is to be deduced more

[1] *Annalen*, 1864, cxxxii. 82.

correctly and consistently from the oxides than from the chlorides. It appears therefore that the precaution formerly exercised in the use of the oxides was excessive, these compounds being systematically avoided as means for determining the valency of the elements contained in them, for fear lest a double union between the atoms of oxygen should lead to erroneous conclusions.

It must, however, be remarked that in the compounds which the elements O, S, Se, Te form amongst themselves, the more negative element appears to be divalent, while the more positive element is hexavalent. Since, as far as we know at present, oxygen forms the electro-negative constituent in all its compounds, therefore its hexavalent nature cannot easily be perceived. The formation of ozone may perhaps serve as an indication of this property, for in its production molecules are obtained containing more than two, in fact, very probably three atoms (compare § 101).

By recognising that S, Se, and Te may be hexavalent, and especially in their compounds with oxygen, it is possible to regard a large number of its compounds as atomic, which could formerly only be considered as molecular compounds; the following examples will serve to illustrate this statement.

The compounds produced by the combination of sulphuric acid (H_2SO_4) with one and two molecules of water may be explained to be atomic compounds. The first of these, viz., $SO(OH)_4$, is known to have been obtained in a crystalline form, and the formation of the second of these, $S(OH)_6$, is attended by the maximum of contraction (Ure), and on electrolysis is decomposed into H_6 and SO_6 (Burgoin).[1]

It is generally recognised that many sulphates and other salts retain some of the water combined with them more strongly than the rest. The water so retained was styled saline water by Graham,[2] and halhydrate water by Liebig,[3] since this molecule of water is expelled when the salt unites with another to form a double salt, for example—

$$(MgSO_4,H_2O + 6H_2O) + K_2SO_4 = (MgSO_4,K_2SO_4 + 6H_2O) + H_2O.$$

[1] Gmelin Kraut, *Handb.* i. 206. [2] *Annalen*, 1835, xiii. 144; 1836, xx. 141.
[3] *Ibid.* 1838, xxvi. 144.

Erlenmeyer [1] has sought to explain this phenomenon in a very ingenious manner, by supposing that in these salts the acid and base are both combined with the saline water as semi-hydrates, thus :—

$$HO—Mg—O—SO_2—OH + KO—SO_2—OK =$$
$$KO—SO_2—OMgO—SO_2—OK + H_2O.$$

But magnesium sulphate may be supposed to be the salt of the acid, $SO(OH)_4$, and the formation of this double salt would then be explained as follows :—

$$MgO_2—SO—(OH)_2 + OSO—(OK)_2$$
$$MgO_2—SO\begin{matrix}O\\ \diagup\diagdown\\ O\end{matrix}SO—(OK)_2 + H_2O.$$

§ 180. In the seventh family, containing Mn in the first group, and F, Cl, Br, and I in the second group, the members of the second group are monovalent in their compounds with more positive elements, and also with the elements of the sixth family, with the single exception of oxygen. In their compounds with one another these elements are monovalent [2] only in those compounds which are not decomposed when converted into vapour, whereas in those compounds which are decomposed in the conversion into the gaseous state, *e.g.* ICl_3,[3] the less negative element appears to be polyvalent. Whether the compound IF_5, discovered by Gore,[4] may be volatilised without decomposition is not known at present. The maximum valency in these compounds has not yet been fixed. Chlorine, bromine, and iodine are heptavalent in their compounds with oxygen, as is shown by the composition of their highest oxides and hydroxides, the so-called peracids and their salts; these contain two atoms of one of these elements combined with seven atoms of oxygen, or an equivalent number of hydroxyl groups or their metallic derivatives.

Since for a portion, at least, of the oxyacids and salts of this group the rule holds good that the number of the hydroxyl groups is equal to the number of hydrogen atoms in

[1] *Ber. d. deut. chem. Ges.* 1869, 289. [2] Compare § 91.
[3] O. Brenken, *Ber. d. deut. chem. Ges.* 1875, 487; and P. Melikoff, *ibid.* 490.
[4] *Jahresber.* 1871, 224.

the hydride, viz. one, so if necessary the old views described in § 112 may be retained, in which these elements are monovalent in their combinations with negative atoms, and therefore the formula of perchloric acid would be written as a chain of atoms linked together in the following manner :—

H—O—O—O—O—Cl.

By writing the formula in this way, all analogy between perchloric and permanganic acid is destroyed, since the latter could not be written in a similar manner, inasmuch as manganese, at any rate, is polyvalent.

At the same time, the heptavalency of these elements enables one to give a uniform explanation to an entire series of compounds, which otherwise must be regarded as molecular compounds ; thus, for instance, the hydrates of perchloric acid would be formulated as follows :—

ClO_4H, ClO_5H_3, ClO_6H_5,
or $ClO_3(OH)$, $ClO_2(OH)_3$, $ClO(OH)_5$.

The intermediate hydrate has been found to yield the other two on distillation, and if these compounds were molecular compounds of water and $HClO_4$, then in all probability water would distil over, whereas ClO_5OH distils over, and $ClO(OH)_5$ remains behind ; [1] a fact which is quite in accordance with the general rule that hydroxyl groups reduce the volatility. The crystalline periodic acid and its silver salts are represented by the following formulæ :—

$IO(OH)_5$, $IO(OH)_2(OAg)_3$, and $IO_3(OAg)$.

Both these salts behave to one another in a manner analogous to that exhibited by the normal phosphate and the metaphosphate.

According to J. Thomsen [2] hydrochloric acid in aqueous solution is probably $ClOH_3$, a composition which could only be understood when chlorine is supposed to be polyvalent. If hydrochloric acid be H_2Cl—OH, then the anhydrous chlorides,

[1] The purity of the hydrate varies with the pressure under which it is distilled, *vide* Roscoe. *Annalen*, 1862, cxxi. 346.

[2] *Pogg. Ann. Jubelband*, 1874, 135.

and the anhydrous sulphates, perchlorates, &c., must be anhydride compounds, analogous to the metaphosphates obtained from the acid phosphates.

If it be also accepted that fluorine may under some circumstances be polyvalent, then the numerous compounds of hydrofluoric acid and its salts, which are usually regarded as molecular compounds, may be viewed as atomic compounds. For example, hydrofluosilicic acid, H_2SiF_6, the fluosilicates, and the corresponding compounds in which silicon is replaced by titanium, zirconium, or tin, may be explained in this way. If hydrofluoric acid be supposed to have a formula similar to that assigned by Thomsen to hydrochloric acid, then the water with which some of these compounds crystallise may be included in the atomic linking, for instance, in the compounds which are isomorphous with one another, and have the following general formulæ, in which M denotes either magnesium, zinc, cadmium, nickel, cobalt, manganese, iron, or copper: $MSiF_6$, $6H_2O$, $MTiF_6$, $6H_2O$, $MZrF_6$, $6H_2O$, $MSnF_6$, $6H_2O$, and $MPtCl_6$, $6H_2O$.[1] Much may be said in favour of this view; more especially is support to be found in the fact that hydroplatinic acid, H_2PtCl_6, $6H_2O$[2], is a well-defined crystalline compound.

The fact that fluorine and chlorine must be considered as polyvalent in their combinations with hydrogen and the metals, for which otherwise there is no necessity, must be regarded as a weighty objection to the acceptance of all these formulæ.

§ 181. In the eighth family, consisting of three groups of the following elements: Fe, Co, Ni; Ru, Rh, Pd; Os, Ir, Pt, a difference of behaviour in their combinations with positive and negative elements has not been proved. This arises from the fact that scarcely any compounds are known containing well-defined positive elements; however, a great number and variety of compounds containing negative atoms and radicals are known. In these the number of negative atoms or equivalents, and consequently the apparent valency, varies between 2 and 8. The existence of several chlorides and oxides, &c.,

[1] H. Topsoë, Strecker's *Jahresber.* 1868, 276.
[2] R. Weber, *Pogg. Ann.* 1857, cxxx. 443.

which give up a part of their chlorine or oxygen easily, indicates that this variety may be due to a low intensity of all or some of the combining powers of these elements. As in the sixth and seventh families, and to some extent in the fifth family also, the number of chlorine atoms with which the members of this family combine is not seldom smaller than the amount equivalent to the oxygen in the oxides; the maximum in the former is four, and in the latter eight. There can be no doubt that the metals ruthenium and osmium are octovalent in the two oxides RuO_4 and OsO_4, compounds which are volatile without decomposition. From analogy it might be expected that Rh, Pd, Ir, and Pt would also be octovalent, although these elements can only combine with two, three, or four atoms of chlorine, and the compounds containing the equivalent quantities of oxygen are not very stable. The existence of the hydroplatinic acid, H_2PtCl_6, mentioned above, and its salts, K_2PtCl_6, &c., can scarcely be regarded as proof of the octovalency of platinum. It is a matter of considerable doubt whether the metals Fe, Co, and Ni are also to be regarded as octovalent. The salts of ferric and cobaltic acids show such a great resemblance to those of manganic, permanganic, and ruthenic acids that they may, at all events, be considered as indications that these metals possess a high valency. The cobalt ammonium compounds may be regarded in a similar manner, for instance, purpureocobaltic chloride $(NH_3)_5CoCl_3$ may be considered as containing five hydrogen atoms of five ammonium groups, replaced by an atom of cobalt, which is also combined with three atoms of chlorine.

Fe, Co, Ni, and also Mn are known to form compounds isomorphous with the divalent elements Zn, Mg, Ca, and Cu, and further, Pt forms compounds isomorphous with the tetravalent elements Zn, Sn, Ti, &c. It is an important, but at the present an unanswerable question, whether these elements enter into the compounds in question, viz. the sulphates, carbonates, &c. combined with two and four combining powers respectively, *i.e.* as partially saturated atoms, or whether the low valency of these atoms, as also the divalency of zinc, and the tetravalency of tin, may not arise from a double union of these atoms themselves.

§ 182. The conclusion that the valency of an element may vary according as the element with which it combines is electro-positive or negative, necessitates further consideration. This, although not generally true, is certainly true of the members of the second group of the families V. VI. and VII. In this way an answer is found to the question raised in § 159, as to whether the chemical value of an atom is a magnitude influenced by causes external to it, or whether this value is an invariable property of the atom itself.

That the valency of an element is closely related to its electro-chemical behaviour, is shown by the series of elements from sodium to chlorine or even to potassium, the compounds of which with the electro-positive element hydrogen and the electro-negative element oxygen have the following formulæ.

Na	Mg.	Al.	Si	P	S	Cl	K
?	?	?	SiH_4 Tetra-	PH_3 Tri-	SH_2 Di-	ClH Mono-	?
Na_2O Mono-	Mg_2O_2 Di-	Al_2O_3 Tri-	Si_2O_4 Tetra-	P_2O_5 Penta-	S_2O_6 Hexa-	Cl_2O_7 Hepta-	K_2O Mono-

Thus it is seen that whilst the electro-positive character of the element steadily decreases throughout the series from sodium to chlorine, the valency toward the electro-negative element oxygen increases by a single unit from element to element. On the other hand from chlorine to silicon, the middle member of the series, the valency toward the electro-positive element hydrogen increases step by step, whilst the elements themselves gradually become more and more positive. The chemical value of an element, therefore, is greater toward those elements most nearly allied to it, and smaller toward the elements to which it exhibits the greatest contrast. Since it has been observed that the greater the contrast between two elements the stronger is their affinity for one another, this remarkable behaviour of the elements may be expressed as follows: 'Elements of variable valency exercise the smaller valency when combining with those for which they have the greater affinity, but the higher valency when uniting with those for which they have but small affinity.' It would appear

therefore, that affinity is able to make up in quantity what it lacks in intensity, concentrating itself, as it were, on a single point, when the elements are most dissimilar, whilst with elements more nearly allied affinity extends its action and consequently loses in power. An explanation of these phenomena cannot be given until a more thorough understanding of the nature of affinity itself has been arrived at.

It is not a little remarkable that in the fourth, fifth, sixth and seventh families the sum of the valencies toward electropositive and negative elements is eight, which is equal to the highest valency observed in the case of any given element, (Ru Os).

	IV. C, Si, &c.	V. N, P, &c.	VI. O, S, &c.	VII. F, Cl, &c.
+ :	4	3	2	1
− :	4	5	6	7
Total .	8	8	8	8

But great difficulties would arise were we to assume, however plausible the supposition, the existence side by side of these eight affinities.

§ 183. By the acceptance of a higher valency for some elements, we are in a position to consider as atomic many compounds which could not formerly be regarded as such. It must not, however, be forgotten that considerations of this character are based upon very uncertain grounds.

All our former views on this subject were based upon Avogadro's hypothesis, and the molecular weights determined by its aid. Since we have no means of determining the molecular weights of solids and liquids equivalent to Avogadro's hypothesis, consequently when we apply conclusions drawn from the study of gases and vapours to solids and liquids, the deductions at once pass beyond experimental control. We then move in a purely hypothetical sphere, in which the boldest flights of the imagination are without bounds, and, despite this, there still remain many compounds which cannot even be forced into the types extended in this way.

It is certainly not impossible that at some time the existence of these numerous compounds will be found to be due to the same causes as those producing the compounds which we at present consider as atomic. At present it is, at all events,

convenient, and may be always necessary, to retain the distinction between atomic and molecular compounds, a distinction to which chemists have from the earliest been accustomed, but to which Kekulé, after the discovery of the law of atomic linking, gave a more restricted meaning.

If we consider the means we possess to distinguish the two forms of combination in quantitative proportions, then we shall soon discover that this distinction cannot, with our present knowledge, be strictly carried out. If, however, the extreme cases alone are considered, then many of the means of distinguishing these compounds appear to be satisfactory, but between these extreme cases there are many in which these methods are of no service. Further, the fact that compounds which one chemist regards as decidedly atomic, are viewed by other chemists as undoubtedly molecular compounds, may be considered as sufficient evidence that a thorough means of distinguishing these compounds has not yet been discovered.[1] It is customary to consider as molecular additions, first of all, the compounds of the most distinct substances with water of crystallisation, many double salts, and, in general, those combinations in fixed quantitative proportions, formed by the crystallisation of different substances together, in which the properties of the constituents remain as unchanged as in mixtures in varying proportions, formed by solution, absorption, &c., which it is customary to speak of as physical combinations, in contradistinction to chemical combinations formed in fixed quantitative proportions.

But it has already been shown that many compounds of this character may also be regarded as atomic compounds. On the other hand, it must be remembered that many of these compounds stand in the closest relationship to the so-called physical combinations; thus, for instance, the solution of a salt in water with the amount of water with which it crystallises. For, in the case of many salts, *e.g.* with Glauber's salt and sodium carbonate, by a slight increase in temperature

[1] A. Naumann, in a brochure entitled 'Ueber Molekülverbindungen nach festen Verhältnissen,' Heidelberg, C. Winter, 1872, criticises the means which it has been proposed should serve to distinguish molecular compounds. Comp. Will's *Jahresber.* 1864, 9.

the water of crystallisation may be converted into water of solution, which then holds in solution a large portion of the salt, which is either anhydrous or combined with less water than before, and prevents its crystallising out. It is highly improbable that a small change in temperature should have suddenly brought other forces into play; everything indicates rather that the force which serves to unite the water in a crystalline salt is identical with that which retains it in solution.

§ 184. It certainly remains doubtful whether these phenomena, atom linking, combination with water of crystallisation, solution, &c., are not all, as was supposed by Berthollet, and carried out more completely by Kekulé[1] in his examination of molecular compounds, to be attributed to different modes of action of one and the same force inherent in the atoms themselves. Kekulé started from the supposition that the atoms combined together in a molecule are capable not only of acting upon one another, but also of exerting attractions of a greater or less force upon the atoms of other molecules brought into proximity to it. For, if this were not the case, then the atoms combined together in a molecule could not exert any action upon atoms outside that molecule, and would never combine with such, and consequently a decomposition of the molecule by the action of the affinities of other molecules or atoms would be altogether impossible, which is contrary to experience.

If, in conformity with the above, it be supposed that the atoms of two or more molecules re-act upon one another when these molecules are brought in sufficiently close proximity to one another, then many possibilities may arise. If the forces of attraction exerted on an atom in a molecule by those in another molecule be more feeble than the forces which retain it in its position, then no change can take place. If, however, the force exerted by the atoms of the latter molecule be the greater, then the atom in the first molecule must, owing to the greater force, change its place, and on leaving the first compound enter into a new one. In this case, therefore, a partial or complete decomposition of the first molecule will

[1] *Vide* the references given in § 166.

take place the constituents of which go to form new compounds, in accordance with forces acting upon them.

But supposing the forces by which the atoms of the different molecules react on each other are not sufficiently great to produce a reciprocal change of the atoms, or bring about a chemical decomposition, yet the sum of all these attractions may suffice to hold the molecules in close proximity to one another, and thus produce a species of combination of the molecules.

If the external conditions change, more especially the temperature, then it may happen that the relation of the affinities will also be changed, and a chemical decomposition, or a change in position of the atoms, take place.

These views are chiefly supported by the observation that after the decomposition of the first compound the atoms and molecules are frequently distributed in the two molecules differently from what they were before the action took place.

For example, many chlorides, such as those of zinc, magnesium, and aluminium, form crystalline compounds with water, which on heating evolve hydrochloric acid and leave residues of the oxides, hydroxides, or oxychlorides. It is very probable that these compounds owe their formation to the attraction which the metal has for the oxygen on the one hand and that of the chlorine for the hydrogen on the other, attractions which at the ordinary temperature are not sufficient to produce a complete decomposition.

Many examples of such combinations followed by decomposition might be cited.

§ 185. By extending this conception somewhat, then molecular additive compounds are apparently analogous to all other molecular aggregations, which are usually considered to be produced by the action of a special force of cohesion or adhesion.

It is certainly clear that the molecules must not necessarily be different, in order that they may enter into a species of combination. For instance the oxygen of a molecule of water will exert a certain attraction upon the hydrogen contained in another molecule of water, but this attraction cannot bring about a double decomposition unless aided by special external

circumstances. The existence of such attractions affords an easy explanation of the union of particles into solid masses, in fact of those phenomena, the cause of which is usually attributed to the action of the force of cohesion.

As some atoms are more influenced by this attraction than others, so the molecules, in which these atoms are not quite symmetrically arranged, will present certain sides to one another and assume fixed directions and positions with regard to each other. But supposing all the molecules of a substance to be placed and directed in a fixed regular manner to one another, then a difference in different directions will be observed in the resulting mass of the substance; in other words, the substance would attain the properties of a crystalline medium.

The crystallisation of simple bodies, the crystallisation with water, the formation of double salts by the union of different closed molecules, and in general the formation of molecular addition compounds of all kinds, and many other phenomena, when regarded from this point of view appear to be the results of one and the same kind of action. These combinations are accordingly produced not like the true chemical compounds by the chain-like joining of atoms, as a result of which each atom can bind a fixed and limited number of other atoms, but owe their production to the sum of the attractions which the atoms combined in a molecule are able to exert beyond the limits of the molecule. The prime cause of both kinds of compounds is one and the same, viz., the affinity of the atoms, and it appears unnecessary, therefore, to require the existence of other special molecular forces to explain the phenomena of cohesion, adhesion, capillarity, &c.

PART III.

DYNAMICS OF THE ATOMS.

X.

CHEMICAL CHANGE AND ITS CAUSES.

§ 186. The compounds produced by the union of elementary bodies are not to be regarded as unchangeable, but rather as subject to the greatest possible variety of changes, which without exception can be attributed to the movements of material particles. These changes must therefore be considered as forming a branch of the study of mechanics, a view held many years ago by Berthollet. Since in accordance with the views held at the present time matter is composed of ultimate particles consisting of molecules, and these again of atoms, the changes which bodies undergo are of two classes, according as the composition of the molecules, so far as concerns their constituent atoms, is affected or not. The study of these changes falls consequently into two divisions: in the first, forming the dynamics of the molecules, those changes and phenomena are investigated which are determined by the movements and positions of the molecules alone: in the second, constituting the dynamics of the atoms, are studied those phenomena which are dependent upon the mutual action and motion of the atoms, upon which again the nature of the molecules themselves is dependent.

The subject of molecular mechanics may, like ordinary mechanics, be divided into, first, Statics, embracing the study of the equilibrium of molecules; secondly, Kinematics, the study of their movements; and thirdly, Dynamics, the study of the forces of the molecules. A corresponding series of

divisions may, in accordance with the views of Berthollet, be made in the mechanics of the atoms: first, Statics, the study of the equilibrium of the atoms; secondly, the forces and movements of the atoms, which cannot well be further subdivided, but may suitably be styled the Dynamics of the atoms, which is more usually spoken of as the doctrine of chemical change. Inasmuch as the movements of the molecules must affect the relative position of the atoms composing them, and, on the other hand, the movements of the atoms influence the condition and behaviour of the molecule, there are many phenomena which will require for their elucidation the aid of both these branches of science. Nevertheless, a fairly well-defined boundary may be drawn between the two, as soon as, in the study of any given phenomena, the important and essential can be discriminated from that which is merely accessory and non-essential.

§ 187. Molecular mechanics embraces the study of all those phenomena in which the nature, number, and linkage of the atoms composing the molecules remain unchanged; the movements of the atoms themselves may, however, undergo considerable changes. The mechanics of the atoms is concerned with the study of such phenomena as are dependent upon the nature, number, and mode of linkage of the atoms composing the molecules.

The phenomena of cohesion, capillarity, adhesion, changes of the state of aggregation, fusion and solidification, crystallisation, evaporation, vaporisation and condensation, solution, absorption, diffusion, friction and analogous changes belong, therefore, to the study of molecular mechanics. The mechanics of the atoms treats of the atoms themselves, and the statics embraces the conditions of equilibrium of the atoms, as laid down in the two preceding books, whilst the subject of this division of the work will be the dynamics of the atoms, or the doctrine of chemical change.

Between the mechanics of the molecules and of the atoms there is still a wide field, which may equally well be considered as belonging to one or the other division, and may be regarded as forming that branch of study which has for its object the investigation of the dependence of the mechanics of the mole-

cules upon those of the atoms. This forms that extensive field of knowledge known as physical chemistry, which has for its object the investigation of the interdependence of the physical properties of bodies and their stochiometric composition, as also of the linking of the atoms in their molecules. This branch of science should, from a strictly theoretical point of view, belong more specially to physics than to chemistry. For assuredly the investigation of the physical properties of substances and their causes is the province of physics. As a matter of fact, the opposite has obtained. This has arisen from the fact that the physical properties are dependent upon the atomic linkage, and hence their study is eminently adapted for the investigation of the arrangement of the atoms obtaining in the molecule. It is, however, to be expected that, in the future, physical investigations of the material nature of substances will, as one of the most important fundamental constants, receive more and more attention; and, consequently, in this way these investigations will gradually come to be regarded as a branch of physics.

§ 188. The division of the material between atomic and molecular mechanics is, on the whole, a matter of no great difficulty: to the former belong all phenomena regarded as chemical in the narrower signification of the term; to the latter physical phenomena. But, just as the boundary between physics and chemistry cannot be sharply defined, so, in many respects, does the boundary between atomic and molecular mechanics become uncertain. In cases of changes in the stochiometric composition, there is, as a rule, no difficulty in deciding whether the change in question be a chemical or a physical one. Still, even here, many cases occur of a doubtful nature, more especially in connection with the cases of molecular aggregations, *e.g.* the compounds with water of crystallisation, and the like, which may either be regarded as produced by the juxtaposition of molecules, or, with equal justice, as true chemical compounds. Certainty may also be felt as to the classification of cases of isomeric and allotropic modifications. The conversion of white phosphorus into the red modification may be regarded as a chemical change, brought about by a change in the composition of the mole-

cules, formed of unchanged atoms. The difference between amorphous and crystalline sulphur may be explained in a similar manner; whereas the different crystalline forms of sulphur might rather be attributed to different forms of aggregation of similar molecules, of which the one represents the state of equilibrium at one temperature, the other a like condition at a higher temperature. A similar statement applies to the case of the modifications of calcium carbonate; arragonite crystallising from water at a higher, and calc-spar at a lower temperature.

As a rule, the allotropic modifications produced by change of external conditions, *e.g.* of temperature, may be considered as arising simply from the different mode of grouping unchanged molecules, and therefore they resemble the so-called physical isomerides, which revert to their original state when brought under the normal conditions, or by some other trivial influence, such as affects the conversion of the yellow modification of mercuric iodide into the red, or *vice versâ*. The two forms of benzophenone afford an instance of physical isomerism; the conversion of one form of it may, in fact, be effected by simple contact with the crystal of the isomeride. But between these cases of difference in physical properties, and those in which the chemical composition remains the same, the physical and chemical properties are so distinct that the substances are said to be chemically isomeric; there are many instances resembling both, forming, as it were, a bridge between the two extremes; hence it becomes impossible to draw a hard and fast line between physical and chemical isomerism, or physical and chemical allotropism.

§ 189. The chemical changes forming the subject of atomic dynamics may be classed as follows:—

1. Formation of molecules by direct union of atoms (pure synthesis), or
2. Their decomposition into atoms.
3. Several molecules may unite to form one single molecule (addition), or
4. One molecule may be decomposed into several, which may either be similar or dissimilar.

5. A molecule may lose one or several of its component atoms, or

6. May take up other atoms.

7. The withdrawal and simultaneous replacement of an atom, which generally takes place in such a way that the replacing atom is equivalent to the atom replaced, and usually takes its position (substitution).

8. The atoms in the molecule may change their mode of linkage (isomeric change).

These are the chief modes of chemical change, but usually several of them occur simultaneously, rendering in this way the resulting phenomena more or less complex.

The simplest cases are by no means the most frequent; more especially is this the case with regard to the two first modes of action, which seldom occur, owing to the conditions under which our observations are made. The formation of a compound from its elements, or its decomposition into these, is not necessarily identical with the formation of their molecules from isolated atoms, or their resolution into atoms; inasmuch as the molecules of elements (*vide* § 18) consist, as a rule, of several atoms, and are therefore compounds, distinguished from other compounds by the fact that they are composed of similar atoms.

As will be shown later on, it is only at very high temperatures that the decomposition of compounds into isolated atoms, or the formation of compounds from these again, can take place. It has not yet been demonstrated whether, at temperatures above 3000°, water is resolved into the atoms of its elements, thus:

$$HOH = H + H + O,$$

or whether this change is effected in the manner expressed by the following equation:—

$$2HOH = 2H_2 + O_2.$$

In the case of some elements, as, for instance, mercury and cadmium, we know that they form, in the gaseous state, monatomic molecules, and can, therefore, enter into combination without a previous resolution of their molecules into

atoms. But even in those cases where such an element combines directly with a molecule of another element, *e.g.*:

$$Hg + Cl_2 = HgCl_2,$$

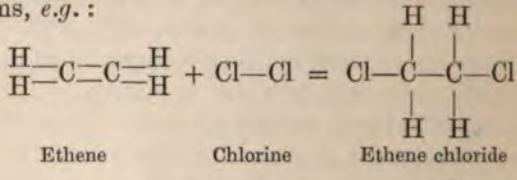
then combination and decomposition take place simultaneously, for the atoms of the second element, which in this instance is chlorine, are separated from one another, thus:

$$Hg + Cl—Cl = Cl—Hg—Cl.$$

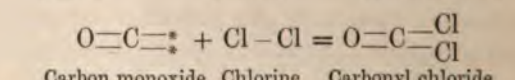
In the same way the decomposition of a compound is accompanied by the production of a compound:

$$I—Hg—I = Hg + I—I.$$

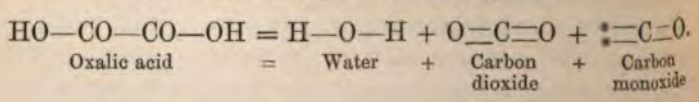
It more frequently happens that molecules are produced by the union of molecules than by the union of isolated atoms, and also that molecules are resolved into others rather than into atoms, *e.g.*:



Ethene Chlorine Ethene chloride



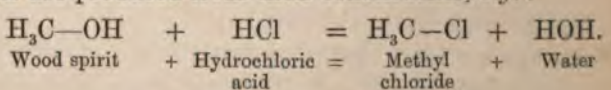
Carbon monoxide Chlorine Carbonyl chloride



Oxalic acid = Water + Carbon dioxide + Carbon monoxide

But, in these cases also, affinities are simultaneously combined and set free; at any rate, this may be supposed to occur with chlorine in the second of the above-mentioned instances.

By far the most frequent form of chemical change is, as was pointed out by Gerhardt,[1] that of double decomposition, in which two or more molecules mutually exchange elements in such a manner that both are decomposed, and new compounds are produced from their constituents, *e.g.*:



Wood spirit + Hydrochloric acid = Methyl chloride + Water

[1] *Traité de Chimie organique*, T. iv. 570, &c.

To this class of decomposition belongs the majority of these cases, which were formerly wrongly regarded as pure syntheses of molecules from isolated atoms, *e.g.* the formation of hydrochloric acid:

$$H—H + Cl—Cl = H—Cl + H—Cl.$$

A double decomposition is frequently preceded by the addition of two molecules, *e.g.* the formation of the arsenic compounds mentioned in § 178:

$$(CH_3)_2AsCl + Cl_2 = (CH_3)_2AsCl_3 = (CH_3)AsCl_2 + CH_3Cl.$$

It is possible that this is the general rule, for we must assume that the molecules must come very close together, in order that the forces producing these reactions (forces which are effective at only very small distances) may come into play.

It is in this way that Kekulé[1] attempts to explain the formation of many bodies which he regards as molecular compounds, *e.g.*—

$$NH_3 + I(CH_3) = NH_3I(CH_3) = NH_2(CH_3) + HI.$$

Many of the compounds regarded as molecular by Kekulé,[2] especially those of nitrogen and its analogues, are now supposed to be true atomic compounds, to which these views can no longer be applied. It is, however, quite possible that molecular additions precede chemical changes more frequently than we at present suppose.

§ 190. The displacement of the constituents of molecules is necessarily accompanied by a change in the mutual attraction or mode of linking of the atoms. The simplest case is that in which the position of the atom displaced is filled by the displacing atom, when in other respects the linking remains unaltered; this appears to occur very frequently, especially in those changes spoken of as simple substitution, and is characterised by the fact that the valency of the atom or radical displaced is equal to that of the atom or radical by which it has been displaced, and further, that the chemical properties of the new substances resemble those of the original as far as is compatible with the relative properties of the displacing and displaced portions.

[1] *Vide* note on p. 315. [2] *Vide* § 166.

That the linkage also changes when several molecules unite to form one molecule is shown in the cases of the formation of ethylene dichloride and of phosgene gas, mentioned in the last section. Similarly in the formation of polymerides, which are simply produced by the union of several similar molecules to form one single molecule, the portions which were at first separate are now united by bonds of union which were previously either unused or otherwise employed. The numerous instances of the changes of a substance into isomerides having the same molecular weight but different properties, can only arise from a change of the position and mode of linking of the atoms, a view which can be substantiated in such cases as have been most thoroughly investigated.

Changes of the mode of linking appear frequently to accompany changes of composition, and in such a manner that the mutual relations of the atoms in the residue are also affected. These cases are often difficult to detect; indications of such changes having taken place may, however, be recognised when, judging from a comparison with those cases analogous in character, the properties of a substance appear to have undergone a change greater than can be explained as resulting from the simple change in composition. Such conclusions are often of an uncertain character.

The solution of the question as to whether changes have taken place in the atomic linkage in any particular case is to be attempted by the aid of those rules and methods laid down in the seventh chapter of this book. The solution of this problem, though difficult, is a matter of necessity, for without a knowledge of the changes taking place in the linkage of the atoms of a molecule, which obtain in a given chemical action, the comprehension and explanation of this particular change must be wanting in completeness.

§ 191. The causes of chemical change are to be sought in part in the molecules themselves, and in part in the atoms composing them, as also in external circumstances, but only so far as the latter exert an influence on the molecules themselves, which influence is dependent upon the nature of the atoms.

Our knowledge of those causes of chemical action which

)endent upon the intrinsic nature of the atoms them-
is extremely limited. We need not, therefore, be sur-
that the material changes constituting, in the restricted
)f the term, true chemical phenomena, which are so
ıtly accompanied by external changes of so marked
rprising a character, should from the first have been
ted to a special and peculiar force, for a long time
as affinity or combining power.[1]

e necessity of explaining chemical action by calling into
ce a distinct force, has been repeatedly contested. Its
ce has been denied on two distinct grounds. First,
was said to be identical with other forces such as the
ıal attraction of matter, gravitation, or with electrical
ion; or, secondly, the power of attraction or action at
nce, *i.e.* the existence of any force acting through space,
nied and considered untenable, the phenomena being
ed by the movement of material particles in the same
ıat the kinetic theory (§ 14) explains the pressure of
which was formerly supposed to be due to action at a
e) by the motion of the molecules.

thollet, as has already been mentioned in the intro-
ı, attempted to explain chemical action by the univer-
raction of matter, whilst Berzelius tried to show it as
lependent upon electrical attraction. The conception
l actions usually regarded as due to attraction are in
the outcome of the movements of the ultimate parti-
ıd that they do not require any special force of attrac-
r their explanation, was current among physicists in
t, and at the beginning of this century, and an attempt
ıde by Le Sage,[2] with at all events but little success, to
chemical phenomena in this manner. Since, in the
y years, consequent upon the development of the me-
ıl theory of heat, the kinetic explanation of phenomena
ecular physics has been gradually preferred to others,
ld appear probable that in the future it will find a

the historical development of the conception of affinity, consult
Geschichte der Chemie, ii. 263, &c.

L. Le Sage, *Essai de Chimie Mécanique*, couronné en 1758 par
ie de Rouen.

further extension in the province of chemistry. The theory of vortex-atoms, connecting an old Cartesian doctrine with a new one by Rankine, founded by Sir William Thomson upon the physico-mathematical investigations of Helmholtz, may form the commencement of such an extension.[1]

According to this theory, atoms are small, but finite systems of matter, which rotate about an endless curve as axis, and which, according to the investigations of Helmholtz, based upon certain hypotheses, possess the peculiar property that their mass cannot be affected by external influences. Although these views promise a great deal, still much requires to be done before a complete kinetic theory of affinity can be established; nor is it at all probable that such a one could be developed without taking into consideration other molecular actions and also electricity. It appears probable that a theory of the so-called action of affinity will be found which will in itself unite the three methods, in which Le Sage, Berzelius, and Berthollet attempted to avoid the acceptance of a special chemical force or attraction.

As long, therefore, as such a general theory of chemical actions is wanting, we may retain the fiction of a force of affinity without in the least being convinced of its reality, just as physicists are accustomed to speak of a positive and negative electrical fluid without in the least wishing to affirm that the electricities are in reality liquids. There can be no danger attending the use of such a hypothesis, so long as no greater importance is attached to it than it can justly lay claim to; it becomes at once, however, a source of danger so soon as conclusions are drawn from it which are not based upon facts. Accordingly, in the following, the actual cause of chemical phenomena arising from the quality of the atoms, will, as a rule, be spoken of as affinity, and treated as a force of attraction, although the author regards the existence of such a force acting through space (however small), from particle to particle, as not even demonstrated.

Opportunities will doubtless offer themselves of assigning

[1] O. E. Meyer, *Kinetische Theorie der Gase*, 244; *vide* also J. J. Thomson *On the Motion of Vortex Rings*. The Adams Prize Essay, 1882. See especially pp. 114 *et seq.*

o their proper place some of those conclusions arrived at by oo free a use of this hypothesis.

§ 192. Whatever affinity may be, whether it is a species of attraction or results from a peculiar form of motion of the particles of matter which we style atoms, it remains for us to investigate its character, and, if possible, to measure its intensity. Although the solution of this problem has been attempted from time immemorial, yet at the present time we are only on the threshold of such a solution.

In the course of time many different forms of affinity have been distinguished from one another, such as simple, double, &c., reciprocal, predisposing, latent, and many others. But these distinctions relate more to the conditions under which the forces come into operation, and to the results of their action, than to the nature of the affinities themselves.

Further, the majority of these distinctions relate to views of the constitution of compounds which are now obsolete, so that we need not further consider this category of affinities which has fallen into disuse.[1]

Further, we need not consider those old attempts to measure the strength of affinity,[2] which were made before the development of stochiometry. The doctrine of Berthollet must be accepted, for this, although developed without a knowledge of stochiometry, and therefore needing a thorough revision, is in the main still correct. What Berthollet styled affinity is now known by another name and is somewhat different from that we now regard as affinity; nevertheless, it is probable that with advancement in knowledge the ideas developed from Berthollet's doctrine will make themselves more and more widely felt.

§ 193. The views regarding the existence of affinity have been specially influenced by the well-known fact that all the external causes of chemical action to be described in § 194 may, and in fact generally do, result from its action. Heat, light, electricity, and every other form of mechanical action, may be produced by chemical action, but only in fixed and

[1] For further information *v.* L. Gmelin's *Handb.* 5 Aufl. 1. cxi. (1852). H. Kopp, *Geschichte der Chemie*, ii. 302–306 (1844).

[2] H. Kopp, *ibid.* 307, &c.

limited quantities. Whilst, formerly, the relationships of chemical to thermal, optical, and electrical phenomena led to the conception of heat, light, and electricity, as being imponderable substances, which could combine in equivalent proportions with the ponderable; just as, at the present time, all these physical phenomena are now, in like manner, considered to be due to the motions of the atoms. Inasmuch as all motions, together with their causes, are subservient either to the laws of the mechanical theory of heat or to the doctrine of the conservation of energy, so also chemical changes now take their place amongst the numerous and diverse phenomena, the united relationships of which were first investigated and explained by that theory, which, although old, has within the last forty years been most brilliantly developed and advanced. The doctrine of the conservation and transformation of energy, more especially that of the equivalence between heat and work, or, in more general terms, between kinetic and potential energy, applies to chemical, as to all other phenomena.

The expectation that with the aid of these laws the entire mechanics of the atoms could be evolved and represented as deductions from a single principle, still remains unfulfilled. Experience has shown in many instances the fallacy of these altogether too sanguine theories, and consequently investigation has once more been forced to seek advancement in the slower but more certain methods dependent upon careful induction. By these methods thousands of reliable, together with many unreliable observations have been made, and form material ready to hand, out of which a well-founded theory of affinity may be raised in the future.

Whatever be the nature of chemical affinity, it is certainly subject to the first law of thermodynamics, according to which law, based upon the fundamental principle of the equivalence between heat and work, in all cases in which work is produced by heat an amount of heat disappears proportional to the work done, and conversely by the same amount of work an equal amount of heat is produced. This statement may be expressed in more general terms as follows: 'That in any body or in any given system of bodies confined

entirely within itself, and removed from all external influences, the sum of its energy remains unchanged in whatever form it may exist.'

Work is here understood to refer to every change in position in a body or system of bodies, effected in overcoming a force opposing such changes; and by energy is meant the ability to perform work.

There are two kinds of energy: (1) that of motion, or kinetic energy; (2) energy of position, or potential energy. All bodies in motion possess kinetic energy, the magnitude of which is represented by half the product of the mass into the square of the velocity. One of the commonest forms of kinetic energy is heat.

Potential energy is only possessed by those bodies which are acted upon by forces tending to produce motion, and therefore to impart kinetic energy to them. The total kinetic energy which a body can attain by reason of the force acting upon it is the measure of its potential energy.

If these conclusions be applied to chemical phenomena then arises the question, to what form of energy does affinity belong? If it be regarded as a species of attraction then the affinity with which two separated atoms tend to attract one another represents their potential energy. When the atoms yield to its influence then the potential becomes changed into kinetic energy, and in such a manner that at every moment the sum of the energies remains constant. The moment the atoms meet then the potential energy is completely converted into kinetic, which as a rule, although not necessarily, assumes the form of heat. If the atoms are to be again separated and brought to their original position, then to produce this change an amount of work is required equivalent to the heat developed in the production of the compound.

If, on the other hand, chemical attraction is not regarded as resulting from a force of attraction, but as the action of forms of motion peculiar to the atoms, the heat of combination is the result not of potential but of already existing kinetic energy, which was not perceptible as heat. The phenomenon is analogous to the condensation of a gas or

the solidification of a liquid, in which the so-called latent heat, heat at least existing partially as kinetic energy, becomes changed into sensible heat, producing a rise in temperature.

When the atoms are to be restored to their original condition, then the kinetic energy which they have lost must be restored to them, for which purpose any other of its forms, or even potential energy, may be used.

Both of these conceptions are in themselves equally justifiable, and whichever view be adopted the fundamental laws of mechanics may still be applied to the elucidation of the nature of affinity. It is, however, important to keep this fact steadily in mind, because theoretical conclusions have been arrived at on the supposition that the first conception was alone correct, and these deductions were regarded as undoubtedly correct although contravened by observation. If, however, we remain thoroughly convinced of the hypothetical nature of this conception, then affinity may without risk be treated and considered as a force of attraction. This conception will be adopted in the subsequent portions of this book, on account of its convenience and simplicity, although the author is inclined to regard the other view as the more correct.

§ 194. The external causes of chemical action are many in kind. Their influence in producing chemical action varies considerably, and in many cases is of the utmost importance in effecting chemical change. In fact, in all probability no chemical change could take place without their co-operation; moreover, the atoms would retain the position of equilibrium once assumed, were it not for disturbances, usually produced by aid of external circumstances. There are many chemical compounds in which the equilibrium of the atoms can be so disturbed by feeble or strong mechanical force as to produce chemical change, in consequence of which other positions of equilibrium are assumed. Heat effects a similar change on a much larger number of bodies, and probably exerts such an influence on all known chemical compounds. This statement applies in such general terms only when heat is understood to mean that which is conducted and communicated to ponderable matter, since radiant heat and light, which are neither theoretically nor experimentally separable, can only under certain

fixed conditions and with certain substances produce chemical changes.

Another powerful agent, perhaps identical with affinity so-called, is electricity, which is capable of decomposing and forming chemical compounds. This holds true more especially of voltaic electricity, whilst free or static electricity appears, as a rule, to act simply in consequence of the heat produced by the discharge. These causes seldom act alone, usually several of them act simultaneously, either supporting one another or completely or partially neutralising each other, so that difficulty is experienced in attempting to distinguish their action and in isolating and identifying their individual effects. It is necessary, however, for theoretical considerations to investigate them and their mode of action individually. As far as time will allow this will be attempted in the following sections, four of which are devoted to the essentially external causes—impact, heat, light, and electricity—and the two remaining ones to the influence of matter considered qualitatively and quantitatively.

XI.

CHEMICAL CHANGES PRODUCED BY MECHANICAL DISTURBANCE.

§ 195. A NUMBER of chemical compounds undergo some form of change, which is produced in them by contact, pressure, impact, shock, or other form of mechanical disturbance. The ease with which this decomposition takes place, and also the phenomena associated with it, differ very considerably. All possible stages of this change are known, from a slow or rapid change of one or a few properties, such as crystalline form, colour, and the like, to a complete decomposition, accompanied by violent explosion and phenomena of combustion. All substances capable of undergoing such changes resemble each other inasmuch as their molecules or atoms are in a state of unstable equilibrium, to which after a disturbance they no longer return. This equilibrium is frequently disturbed by a change of temperature, either by an increase or by a reduction of the same; the action of heat is not in all cases, however, necessarily identical with that effected by a mechanical disturbance. In many cases this state of unstable equilibrium exists only within certain limits of temperature, whilst at other temperatures the equilibrium is completely stable.

§ 196. The so-called allotropic modifications of bodies which are only stable under certain (often very limited) conditions but easily pass into a more stable form [1] under other conditions, afford an example of unstable equilibrium of the molecules and not of the atoms.

The majority of these substances assume two or more crystalline forms, the one forming at a higher, the other at a lower temperature, or on crystallising from different sol-

[1] For examples *vide* O. Lehmann, *Zeitschrift für Krystallographie*, 1877, i. 97.

vents, &c. These forms often exhibit a tendency to remain unaltered under conditions other than those in which they were produced; at times they become mobile and then slowly or suddenly pass into this stable modification. This change may take place either without external cause or owing to a mechanical disturbance; more especially is this the case when touched with a crystal of that modification which is stable under the new conditions.

Examples of this are seen in the case of sulphur, which crystallises at high temperatures in a monoclinic form, and at lower temperatures in a rhombic form; also in the case of mercuric iodide which when heated changes from red to yellow, and in many other substances.

The form assumed by many substances in passing from the liquid state, either of fusion or solution, to the solid state, is determined by contact with a crystal of one or other of their modifications. Generally one only of these forms represents the state of stable equilibrium, the other unstable equilibrium. If both modifications be brought simultaneously into the fused substance or into a saturated solution of the same, then both continue to grow until they come in contact with one another. The unstable passes then into the stable, since it is consumed by crystals of the other. The stable form always melts at the higher temperature as seen in the following examples.

	Unstable	Stable
Benzophenone . . .	26°	49° (Zincke)
Bibromopropionic acid .	51°	65° (Tollens)
Nitrotetrabromobenzene .	60°	96° (V. v. Richter)
Metachloronitrobenzene .	23°	44° (Laubenheimer)
Isohydrobenzoïne diacetate .	106°	118° (Zincke)
Nitrometachloronitrobenzene	36–37°	39° (Laubenheimer)
Tolylphenyl ketone . .	55°	59° (Zincke, van Dorp).

If one of these substances be raised to a temperature considerably above its melting point, and then suddenly cooled, it will, as a rule, assume the less stable form, melting at a lower temperature. Some of these less stable modifications cannot be melted, since they assume the stable condition before the temperature at which they melt is attained, an example

of this is to be found in the case of one of the modifications of isohydrobenzoïne diacetate, observed by Lehmann.[1]

Supersaturated solutions afford analogous cases of conditions of unstable equilibrium of the molecules of liquids; these when touched by a crystal of the substance dissolved, solidify in the form of the modification introduced. It may be regarded as fully established that such solutions do not contain the substance in the form in which it separates out, but in a form differing by the amount of water of crystallisation contained in it.

Solid bodies may also have their molecules in a state of unstable equilibrium, as is seen in the case of Rupert's drops, obtained by the rapid cooling of molten glass.

§ 197. Atoms as well as molecules may exist in a state of unstable equilibrium, from which by impact or percussion they may be made to pass into a more stable state of rest. The greater number of such substances are to be found amongst compounds containing a considerable amount of oxygen, combined with combustible elements. The nitrates, nitrites, nitro-compounds and perchlorates of organic compounds belong especially to this class. These bodies have one feature in common, viz. the oxygen is completely or almost entirely united directly to the nitrogen or chlorine. By reason of their feeble affinity these elements only hold the oxygen in loose combination, whereas the carbon and hydrogen contained in these compounds have a considerable affinity for oxygen. Should the atoms of oxygen be brought within the sphere of attraction of carbon or hydrogen, either by mechanical disturbance or motion imparted to them consequent on a rise in temperature, then a combination with these elements ensues and the union with nitrogen, and chlorine is dissolved.

The decomposition of these and allied substances is, therefore, completely analogous to that of gunpowder or similar explosive mixtures, from which it differs simply in the fact that in the latter combustible material is mechanically mixed with the nitrates, chlorates, &c., which contain the oxygen, and is not therefore contained in one and the same compound. There still remains a larger number of unstable compounds

[1] *Loc. cit.* 126.

containing either no oxygen or no combustible elements. The compounds of chlorine and oxygen afford examples of this class, more especially hypochlorous and chlorous anhydrides, also the monobasic form of perchloric acid, $ClO_3.OH=HClO_4$,[1] further the anhydride and acid chloride of permanganic acid; again the compounds of nitrogen with a large amount of oxygen (nitric pentoxide), together with the compounds of nitrogen, with sulphur, selenium, chlorine, bromine, iodine, with copper,[2] silver, gold, and finally the organic diazo-compounds. The atoms in these compounds are also in a state of equilibrium more or less unstable and hence pass easily into more stable forms of combination.

From the standpoint of the older conceptions, according to which the elements in a free state consist of isolated atoms, the decomposition of many of these compounds into their elements was quite incomprehensible and inexplicable. No reason could be assigned why in a compound of nitrogen and chlorine, or nitrogen and sulphur, the union should be dissolved by simple mechanical disturbances. Even when the affinities of these elements to one another are feeble, still the existence of a force sufficiently great to overcome this must be demonstrated; the necessity for this is made all the greater by the fact that the decomposition is frequently accompanied by explosion and by a considerable development of heat. These phenomena can now be easily explained by the force of attraction which the atoms of one and the same element have for one another. When, for instance, nitrogen chloride, NCl_3, decomposes into free nitrogen, N_2, and free chlorine, Cl_2, this takes place because the affinity of nitrogen for nitrogen, and chlorine for chlorine, is greater than that of nitrogen for chlorine. From one compound two others are produced, in which the elements are more strongly united than in the former,

$$NCl_3 + NCl_3 = N_2 + Cl_2 + Cl_2 + Cl_2.$$

[1] The crystalline acid $ClO_3H_3=ClO_2(OH)_3$, and that obtained by evaporation of the aqueous solution, probably $ClO_6H_5=OCl(OH)_5$, are less explosive.

[2] Not exploded by percussion, but by heat. In the case of some of the other compounds mentioned explosion by percussion has not as yet been observed.

The decomposition of the other compounds mentioned above and many similar ones may be explained in like manner, and to these in all probability the majority of explosive diazo-compounds must be added, the decomposition of which is probably due to the fact that their groups of two nitrogen atoms, —N=N—, suddenly change into free nitrogen, N≡N.

§ 198. If the products of decomposition of a liquid or solid compound are entirely or partially gaseous, then the decomposition may be accompanied by an explosion, often associated with a considerable evolution of heat. Whether an explosion takes place or not, depends not only on the material nature of the decomposing substance, but also upon the external conditions under which the decomposition takes place, more particularly upon the nature of the external cause, by which the equilibrium of the atoms is disturbed and on the hindrances offered to the evolution of the gaseous products of decomposition.[1]

Explosions are, as a rule, produced by impact and percussion more easily when these act rapidly and powerfully; still they are not entirely determined by the mechanical movement of the impact. The rapid impact of a small, hard mass, acts better than that of a much larger mass moving at a lower velocity, or than a much softer substance. In many cases the effects of impact may be produced by heat, in others not. Many substances, for example, glyceryl nitrate, burn quietly when ignited, whilst percussion causes them to explode violently. It is well worthy of remark that undulatory motions and other periodic disturbances, even when of low intensity, easily produce explosions. Every substance to be exploded by these means requires a certain velocity of vibration. Iodide of nitrogen, for example, does not explode when placed on a string or plate producing a low note, but does so with one emitting a high note. The communication of disturbance from an exploding substance to an explosive substance does not always cause the

[1] The literature of this subject is spread through a large number of periodicals. Amongst later works those of Abel, Nobel, Champion, and Pellet must be specially mentioned. Berthelot, Thomsen, Springmühl and other investigators have given special attention to this subject.

latter to explode. Whether this takes place or not, depends not alone upon the violence of the first explosion, for in many cases a small quantity of a comparatively feeble explosive substance may determine the explosion of another, even when a larger mass of a more powerfully explosive substance would in no way succeed. These differences depend in all probability upon the rhythm of the disturbance produced by the explosions, in such a manner, that the atoms are only set vibrating by vibrations of a fixed wave length, and are consequently further removed than usual from their state of unstable equilibrium and so pass into a state of stable equilibrium. The explosion of different substances by vibrations of different wave lengths may, accordingly, be explained in a manner analogous to that used to explain the sympathetic vibration of different bodies, sensitive flames and the like. Contact with certain substances may also effect a decomposition, although the substances themselves undergo no change. The decomposition of hydrogen peroxide by platinum, gold, silver, manganese peroxide, and other substances, is so effected; potassium chlorate also decomposes at a much lower temperature when in contact with manganese dioxide, ferric oxide or copper oxide, than when heated alone. It is difficult to decide to what extent these so-called contact actions are to be attributed to chemical or purely mechanical causes. The power possessed by animal and vegetable fibres to decompose the compounds of colouring matters and precipitate the colouring matter,[1] is in all probability dependent more upon mechanical than chemical action. Whether a decomposition takes place quickly or slowly, or whether a true explosion, or a violent deflagration is produced, depends upon the resistance the gases produced meet with. With many substances the slightest hindrances, a sheet of paper or the like, suffice to convert an otherwise quiet decomposition into an explosion. Nitrogen chloride, covered with the smallest possible quantity of water, explodes with extreme violence, whereas when freely exposed to the air it explodes with no greater violence than

[1] A striking example of this kind is in the dyeing silk blue from a colourless solution of cyanine acetate. The colour itself shows that the cyanine exists free, and not combined in the fibres themselves.

does the analogous compound, iodide of nitrogen (Abel). The influence of such obstacles depends most probably upon the fact, that the gaseous particles moving with great velocity are reflected back and consequently their motion conveyed to the unexploded particles remaining behind. In the same manner many substances, even those which do not require oxygen for their explosion, explode easily in the air, but not in vacuo.

§ 199. Explosive compounds differ greatly in their stability. Thus, whilst chloride or iodide of nitrogen explode on the slightest touch of a feather, other substances, such as glyceryl nitrate, picric acid or its salts, require for their explosion the powerful stroke of a hammer upon a hard support. These differences are determined by the nature, number and linking of the atoms contained in the compounds. The laws relating to the action of these causes have been, however, but little investigated. In the case of those compounds containing but a small number of atoms of a few elements, *e.g.* nitrogen chloride and nitrogen sulphide, then the nature of the atoms, more especially the strength of their affinities, is of the greatest import. Still the matter is not so simple that one may conclude without further consideration that compounds held together by feeble affinities are necessarily most easily decomposed. The ease with which a decomposition takes place is dependent not only upon the strength of the affinities which have come into action, but also upon the intensity of those which remain unsatisfied.

Consequently the facility with which the decomposition takes place increases with the strength of the unsatisfied affinities and diminishes with the intensity of the satisfied affinities; it is, therefore, determined by the difference between the strength of these opposing forces.

The explosive tendency of a compound depends not only on the nature of the constituents but also upon the position and motions of the constituent atoms.

In complicated compounds, such as the organic nitrates and nitro-compounds, the number of the atoms and their linking has special influence in determining their explosive nature. This influence is, as a rule, the greater, the more nearly the amount of oxygen contained in the compound

approaches the quantity necessary for the complete combustion of the carbon and hydrogen contained in the compound. Glyceryl trinitrate (so-called nitro-glycerine) $C_3H_5(NO_3)_3$ very nearly satisfies this condition, in the decomposition of which, supposing it to take place, as follows,

$$2C_3H_5N_3O_9 = 6CO_2 + 5H_2O + 3N_2 + O,$$

one atom of oxygen, in fact, remains in excess of the quantity required for complete combustion of the carbon and hydrogen. Those derivatives of glycerine, containing a smaller number of nitro-groups, are much less explosive than the tri-nitrate. If this compound be mixed with a nitrate of cellulose (collodion-wool), containing an excess of carbon and hydrogen, the explosion is in this way made still more powerful. Picric acid or trinitrophenol is tolerably explosive; dinitrophenol, which contains less oxygen, is less so; and the mononitrophenol is not explosive. On the other hand, too great an excess of oxygen attached to nitrogen may reduce the explosive power of a compound, although the number of carbon and hydrogen atoms have decreased. Thus nitroform $CH(NO_2)_3$ is explosive, whilst tetra-nitromethane $C(NO_2)_4$ is not explosive. The replacement of a part of the hydrogen in nitro and allied organic compounds by a metal increases, as a rule, its explosive nature. Thus, for instance, potassium picrate $C_6H_2(NO_2)_3OK$ is much more explosive than picric acid $C_6H_2(NO_2)_3OH$.

Remarkably explosive are the so-called fulminates, such as fulminate of silver and of mercury and many other salts of fulminic acid which, as yet, is unknown in the free state. After considerable discussion concerning the constitution of these compounds, a representation has now obtained, in which the metal is attached directly to the carbon, thus:

$O_2N—CHg—CN$;	$O_2N.CAg_2—CN$;	$O_2N—CAgK—CN$
(Mercury fulminate)	(Silver fulminate)	(Silver potassium fulminate)

If these and analogous formulæ do really represent the true atomic linking, then we may conclude that the metals are but loosely combined with the carbon in these compounds.

§ 200. The explosive nature of those compounds, which are thereby resolved into their elements, affords a very welcome proof of the truth of Avogadro's doctrine of the compound

nature of the molecules of many elements. The existence also of those compounds, described in the foregoing paragraphs, containing oxygen combined with combustible elements, furnishes evidence of the truth of the doctrine of atom-linking. For supposing the atoms were not united in a chain-like union with one another, but that each is attached to all the other atoms, then a condition of equilibrium such as obtains in explosive compounds would no longer be possible. For instance, potassium picrate, $C_6H_2N_3O_7K$, would assuredly not be explosive, if the oxygen contained in it were directly united to the carbon; in fact, it possesses this property, by reason of the fact that of the seven atoms of oxygen contained in it, six are combined solely with nitrogen and on explosion they entirely or to a great extent pass into combination with the carbon and hydrogen.

Inasmuch as the explosion of a compound is determined by the affinity of atoms not directly united to one another, the decomposition by mechanical disturbance appears to be very nearly allied to decompositions resulting from the exertion of the affinity of other atoms not contained in the compounds. The explosion of explosive mixtures, *e.g.* that of gunpowder, is in fact dependent on this cause. Such decompositions are scarcely to be distinguished from those of an explosive compound.

XII.

HEAT AS CAUSE AND EFFECT OF CHEMICAL CHANGE.

§ 201. The position of equilibrium of the atoms in compounds is not a position of rest but rather a condition of restricted motion. At all events, the motion contained in bodies in the form of heat is, to a great extent, a motion of the molecules; but although it is theoretically improbable that the atoms should not in their extremely rapid motions amongst themselves displace and move the centre of gravity of the whole molecule, still in all cases in which the intensity of the molecular motion can be measured, it has been shown that this does not completely represent the heat-motion contained in the substance, and consequently a portion of this must be due to the motion of the atoms. A proof of this has been specially established in the case of gases.[1]

If, therefore, the atoms composing a molecule are in motion, it is evident that they, by continued accelerated movement, may, at last, be so far removed from one another as to escape entirely the force of affinity, active only within narrow limits, and be unable to return within the sphere of its action. These theoretical views find a confirmation in the fact, that, as far as our observations go, by far the greater number of chemical compounds can be decomposed by a sufficiently high temperature. In all probability this may hold good for all. This action of heat by which the mutual attraction of the atoms is overcome by accelerated heat-motion alone, occurs apparently only, in those cases, in which compounds are resolved into atoms by exposure to a high temperature. In the majority of instances coming under our

[1] Clausius, *Ueber die Art der Bewegung, welche wir Wärme nennen. Pogg. Ann.* 1857, c. 355–377; Ges. Abh.; 1 Aufl. 235.

notice, the action of heat is accompanied and not unfrequently aided by that of affinity, thus complicating the phenomena and rendering their true interpretation more difficult.

When, for instance, cupric chloride is reduced by heat to cuprous chloride, it is an open question, whether this is due to a simple action of heat or at the same time to affinity; inasmuch as the reaction :

$$Cl—Cu—Cl + Cl—Cu—Cl = Cl—Cu—Cu—Cl + Cl—Cl$$

may take place, if the affinity of Cl to Cl in conjunction with that of Cu to Cu is sufficiently powerful to overcome the attraction, which the two atoms of copper exert upon the two displaced chlorine atoms. The reaction would, therefore, appear to be due to affinity only. On the other hand, quite the opposite view of the case may be taken, viz. that one chlorine atom only is removed by the action of heat alone and that afterwards the isolated atoms and also the unsaturated affinities of the copper atoms combine forming free chlorine and cuprous chloride respectively. It is difficult to decide which of these views is the correct one; in many cases probably the former set of views is a truer representation of the facts of the case, whilst, again, in other instances the latter will be more justly representative.

§ 202. The simplest cases of the action of heat are without doubt those in which the action ceases with the withdrawal of the cause and in such a manner that the substances return to their original condition. To phenomena of this character, whether produced by heat or other cause, the term dissociation has, as mentioned in § 33, been applied by H. Sainte-Claire Deville.[1] The importance of the investigation of these phenomena, as affecting the progress of chemical mechanics, has increased from year to year. Experience has shown that solid as well as gaseous compounds are capable of

[1] The phenomena of dissociation have, since the year 1857, been specially investigated by H. Sainte-Claire Deville, and later on by many other chemists, so that a considerable amount of literature concerned with these phenomena has accumulated. Special attention is drawn to the '*Leçons sur la dissociation, professées devant la société chimique en* 1864.' Paris, 1866, by Deville; also to the chapters on this subject in Naumann's *Thermochemie*. Braunschweig, 1882.

being dissociated, although, as a rule, only when one of the substances produced by the dissociation is a fluid, either gaseous or liquid. And as it is probable that at sufficiently high temperatures all elements are either fusible or volatile, then it must necessarily follow that each and all of their compounds can be dissociated; as a matter of fact, a limited number only can be dissociated, and for the reason that many compounds are not formed again after being once decomposed. These compounds which may be dissociated stand, therefore, in direct contrast to those described in the foregoing paragraphs, which represent the state of unstable equilibrium of the atoms. This contrast is by no means an unconditional one, since under certain conditions dissociated compounds may be prevented from recombining. The phenomena of dissociation have been investigated not only qualitatively but also quantitatively. Qualitatively it has been shown, contrary to expectation, that a considerable number of those compounds formed directly from their elements, and amongst them many stable ones, are capable of dissociation. The special artifices which have frequently been required to exhibit the dissociation in these cases, have been devised and dexterously applied by Deville. Since the dissociated substances reunite at lower temperatures, their existence must therefore be either demonstrated during dissociation, generally at very high temperatures, or their reunion must in some way be prevented. This latter method of demonstration may be applied either by rapid cooling below the lowest possible temperature at which combination takes place, or by separating one of the constituents of the mixture either by diffusion into an indifferent medium or by some other similar method. It has been shown that almost all simple inorganic compounds, containing volatile elements, may be dissociated, such, for instance, as H_2O, CO_2, SO_2, HCl, NH_3, and many others, like the ammonium salts, many carbonates, and the like.

§ 203. Dissociation has been investigated quantitatively as yet only in the case of a small number of compounds, since the experimental investigation, more especially of these cases in which dissociation takes place at very high temperatures, is surrounded by difficulties of no mean character. Hitherto,

those cases only have been investigated in which gaseous products are formed at moderately high temperatures. When the original compound was not gaseous, the quantity of gas produced was determined either by direct measurement or by measurement of the pressure exerted by it; in those cases in which a gaseous compound produced on dissociation gaseous substances, then the quantity produced has been determined by aid of Avogadro's law. The application of this law depends upon the fact that in the decomposition of a gas the number of its molecules changes, and in proportion also its volume or its pressure, and inversely its density, so that from these changes the relative number of dissociated molecules may be calculated.

For instance the molecule $\mathfrak{M}$ of a gas having a density D dissociates into two parts, thus—

$$\mathfrak{M} = m + m.$$

Consequently, under the same pressure, the volume is doubled, and the mean density reduced to a half. If, however, only a fraction (x) in a given volume has undergone dissociation, the N molecules will now have become—

$$N\mathfrak{M} = N(1 - x)\mathfrak{M} + N x m + N x m_1$$

and therefore $N(1 + x)$ molecules in all. Consequently, the increase of volume will be in proportion of—

$$1 : (1 + x).$$

So that the relative increase of the volume gives directly the fraction of the molecules, which have been dissociated. Supposing the molecules to have been resolved not into two parts, but into n parts, then, in a similar manner, the increase of volume will be seen to take place in the proportion of—

$$1 : (1 + (n - 1)x),$$

from which x can be easily calculated.

Since the density is inversely proportional to the volume, then—

$$D : D' :: (1 + (n - 1)x) : 1,$$

$$x = \frac{D - D'}{(n - 1)D'},$$

or when $n = 2$

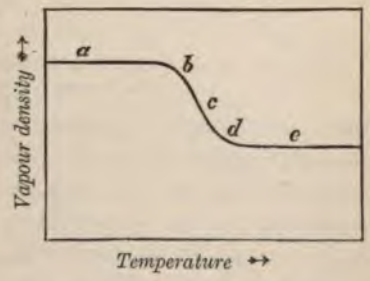
$$x = \frac{D - D'}{D'}.$$

In order to determine what proportion of a gas has undergone dissociation, we have simply to divide the difference between the original density and the density of the gas after dissociation, by this latter quantity. In those instances where the original density cannot be determined directly, it may be calculated, making use of Avogadro's law, from the hypothetical molecular weight by aid of the formula—[1]

$$D = \frac{\mathfrak{M}}{28{\cdot}87}.$$

The correctness of the whole calculation rests entirely, therefore, upon the validity of Avogadro's hypothesis.

§ 204. The cases of dissociation[2] investigated by this method show that the density of gases or vapours capable of dissociation remains constant within certain limits of temperature, then decreases with rise in temperature at first slowly, then more quickly, and goes on slowly decreasing until, above a certain temperature, it again becomes constant. If the densities of such a vapour be represented as the ordinates of a curve, and the temperatures represented by the abscissæ, then a line is obtained which is straight at first, as seen in diagram at *a*, and running parallel to the abscissæ, then assuming the form of a curve, approaching the abscissæ, as at *b*, it then reaches a turning-point *c*, and becomes gradually convex as at *d*, to pass finally into a straight line *e* running parallel to the abscissæ. Such a curve is given by the density of the vapour of amylene hydrobromide, when represented as a function of the temperature. Its density has a constant value of 5·2 until 180° C., and up to this point the curve runs parallel to the axis, then the density decreasing more and more until (as far as it is possible

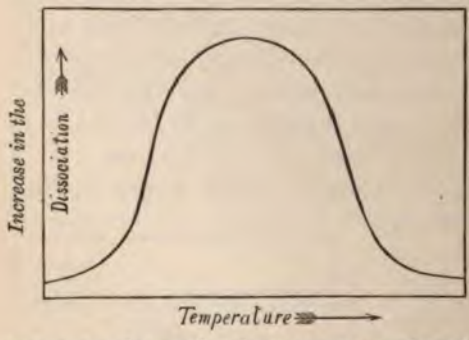


[1] *Vide* § 16.

[2] *Vide* §§ 30–33, also § 18.

to judge from our imperfect observations) a turning-point is reached at 240° C., and when the temperature 360° is reached it assumes the value of 2·6, the curve again becoming parallel to the axis. The density, 5·2, corresponds to the molecular weight, $C_5H_{11}Br$; that of 2·6 represents the complete dissociation into C_5H_{10} and HBr. Many other substances behave in a similar manner; but still for many of these only a part of the curve representing these changes has been experimentally determined.

From the course of the curve described above, it follows that dissociation commences gradually at first, and increases slowly with rise in temperature, then more quickly until a certain point is reached, from which time it again progresses slowly until it gradually becomes complete. The increase of dissociation produced by a given rise in temperature (*e.g.* for 1° C.) becomes, therefore, greater and greater as the temperature rises, until a maximum is reached, and then this increase becomes gradually smaller, at first slowly, then rapidly, and these changes take place in such a manner that the curve representing this increase as a function of the temperature is symmetrical on both sides of the maximum, as shown in the accompanying diagram. The following numbers, representing the dissociation of nitric peroxide, may serve to elucidate the question;[1] the molecular weight of this substance at low temperatures is represented by the formula N_2O_4, and at higher temperatures by the formula NO_2. The calculated density for the first is 3·18, for the latter 1·59. These changes are rendered apparent by the fact that the non-dissociated vapour is colourless, and assumes a dark red colour when completely dissociated, thus the rate of dissociation may be easily estimated. The numbers contained in the



[1] Taken from A. Naumann's *Thermochemie*, 1882, § 117.

following tables require no further explanation than that contained in the titles to each column. The numbers contained in the fourth column represent the mean increase in the dissociation for each degree centigrade, and are obtained by dividing the differences of the numbers in the third column by corresponding differences of the numbers in the first column.

Temp. ° C.	Density D′	Decomposition in per cent. 100 x	Mean increase for 1° C.
		per cent.	per cent.
26·7	2·65	19·96	—
35·4	2·53	25·65	0·65
39·8	2·46	29·23	0·81
49·6	2·27	40·04	1·10
60·2	2·08	52·84	1·21
70·0	1·92	65·57	1·30
80·6	1·80	76·61	1·04
90·0	1·72	84·83	0·88
100·1	1·68	89·23	0·44
111·3	1·65	92·67	0·31
121·5	1·62	96·23	0·35
135·0	1·60	98·69	0·18
154·0	1·58	100·	—
183·2	1·57	100·	—

That dissociation proceeds at first slowly, then rapidly, and again slowly, is sufficiently evident from these numbers. Its commencement cannot be observed, because the vapour condenses to a liquid, the end is easily noted and when near 140° the complete decomposition has taken place.

§ 205. The theoretical investigation of the phenomena of dissociation, based upon the kinetic views expressed in § 201, shows that the motion transmitted to the molecules in the form of heat can only affect the holding together of the atoms in proportion as it is transmitted to these entirely or in part. Its action upon the atoms may be of two kinds, depending upon whether the velocity and consequently the kinetic energy of the atoms is increased, or whether the position of equilibrium, about which they move, be moved in a direction beyond the sphere of the action of affinity, and thus disgregation is increased, or in other words work is done. In all probability both forms of action take place simultaneously. The stronger the affinity holding the atoms together, so much the greater disgregation must obtain and the momentum of the atoms be

increased before the molecules are resolved into their isolated atoms. The energy, therefore, which must be transferred to the molecule to produce dissociation, is a measure of the strength of the affinities, just as the momentum, which must be given to a heavy body, in order that it may be continually withdrawn from the earth's attraction, is a measure of the force of gravity. In fact, it has been observed that those compounds which we, for other reasons, suppose to be held together by the strongest affinities, are those requiring the highest temperatures for their dissociation.

Consequently the temperature of dissociation and the heat communicated to compounds in order to attain this temperature, are quantities of great theoretical import, making their exact determination very desirable. But inasmuch as dissociation takes place within very wide ranges of temperature, the question then arises, at what temperature does the atomic energy exactly suffice to overcome the force of affinity? Since, doubtless, all particles of the undecomposed compound are completely alike, the temperature at which they decompose must be the same for all, so, from a superficial consideration one might be led to conclude that the decomposition and change of density produced thereby must take place suddenly, so soon as the fixed temperature at which all these particles decompose is attained. Such a conclusion would be erroneous in the light of the now accepted theory of the constitution of gases, the theory of molecular impacts, according to which the temperature of all the particles of a gas or vapour is not necessarily the same at any given time, but rather that the temperature of the gas or vapour is only the mean value of the temperatures of the particles composing it. The temperatures of the different particles may differ considerably from this mean value; still, according to theory, small differences must frequently occur, but great differences seldom, so that the further removed a given temperature is from the mean, the smaller will be the number of particles having this temperature. It follows, therefore, that in the vapour of a compound, which decomposes at a given temperature, a certain number of particles will have attained this temperature before the mean temperature as indicated by the thermometer is equal to that

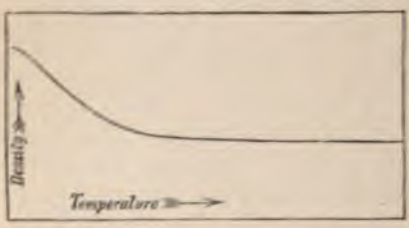
at which the decomposition takes place. The number of decomposed particles will increase the more rapidly the nearer the mean temperature approaches to that at which decomposition takes place. When this point is reached there will always remain a considerable portion of the molecule having a lower temperature, which will consequently not be decomposed. This undecomposed portion will, however, diminish as the temperature rises, at first rapidly, then more slowly until it finally disappears. The particles having the lowest temperature have now attained the temperature of decomposition, just, in fact, as represented in the curve in § 208.

From these considerations it will be seen that the temperature of decomposition is identical with that mean temperature of the gas at which the increase in dissociation has attained the maximum, and this is the point at which the curve of density passes through a turning point. Since equally great differences either above or below the mean temperature are equally frequent, therefore as many particles are hotter and colder than this, it follows that when the mean temperature is identical with the temperature of decomposition, then exactly half the particles have been dissociated. In fact, observations show that the turning point of the density curve corresponding to the greatest increase of dissociation corresponds very nearly to a decomposition of 50 per cent. of the compound. In the case of nitric peroxide, already mentioned, these points are attained at a temperature of about 60° C.

§ 206. In applying Avogadro's law to the study of the phenomena of dissociation of gaseous bodies, a knowledge of the molecular weights, both of the original substance and those of the products of decomposition, is assumed. This determination can only be successfully made in those cases in which the density curve represented in the first figure in § 204 has been completely followed along its entire course. Such a complete examination is, however, often associated with insuperable difficulties; it may happen that the substance condenses at a lower temperature to a liquid, or that it undergoes further decomposition at temperatures above those at which dissociation into smaller molecules takes place. If,

however, the greater portion of the curve is known, and thus far resembles the form described, then there can be no doubt that the phenomenon is one of dissociation. In other cases it must remain doubtful.

By comparing the course of the curve represented in § 204 with that which represents the density of acetic acid vapour compared to air as a function of the temperature (compare § 28), a by no means unimportant difference will be observed. The curves representing the density of those vapours to which the law of Avogadro is applicable, above certain limits of temperature and pressure (*vide* § 29), correspond only to the second half of the first curve; they exhibit a convex side to the abscissae axis which represents the temperature, and run finally in a straight line parallel to this axis. Some observations appear to show that these curves have a turning point;[1] still one portion of the curve is entirely wanting, viz. the upper horizontal part. This may be explained in the manner proposed by Horstmann,[2] by supposing this form of curve to characterise those substances which do not undergo true dissociation, but exhibit an increased density in consequence of a gradual and irregular passage from the liquid to the gaseous state, and within certain limits of temperature contain an abnormal number of particles in a given volume. On the other hand the supposition made by Naumann[3] is also permissible. He assumes that dissociation really has taken place, but the first part has escaped observation by reason of the condensation of the substance to a liquid. If the vapour of acetic acid near to its boiling point (119° C.) consists of a mixture of molecules $C_4H_8O_4$ (D = 4·16) and $C_2H_4O_2$ (D = 2·08), then the vapour produced from the boiling liquid must already have dissociated



[1] For further information on this question *v.* P. Schoop, Tübinger Inaug. Diss. 1880, *Wied. Ann.* 1881, xii. 571.

[2] *Ann. Chem. Pharm.* 1868, suppl. vi. 51,

[3] *Ibid.* 1870, clv. 325.

to the extent of one-third of the whole, for, according to the observations of Cahours[1] at 125° C.—

$$D' = 3{\cdot}20,\ x = \frac{4{\cdot}16 - 3{\cdot}20}{3{\cdot}20} = 0{\cdot}30$$

and at 150° C.—

$$D' = 2{\cdot}75,\ x = \frac{4{\cdot}16 - 2{\cdot}75}{2{\cdot}75} = 0{\cdot}51.$$

Therefore the turning point in the curve must be about 150° C. This supposition is to some extent borne out by observations which are, however, insufficiently exact to permit of dogmatic assertion.

§ 207. In the case of a moderately large number of compounds, it is tolerably certain that their dissociation depends upon the loosening of certain bonds of union which on cooling again become active. For instance, we may represent the dissociation of nitric peroxide as taking place in all probability, according to either of the following schemes :—

$$O_2{\equiv}N{-}N{\equiv}O_2 = O_2{\equiv}N{-}* + O_2{\equiv}N{-}*$$

or

$$O{=}N{-}O{-}O{-}N{=}O \ = \ O{=}N{-}O{-}* + *{-}O{-}N{=}O.$$

Since the nitrogen atom, whether it be tri- or pentavalent, has, at all events, an uneven valency, and both the oxygen atoms an even valency, then at least one valency in the molecule NO_2 produced by dissociation must remain unsaturated, and it is this which, in all probability, is active in effecting the reunion. It is, however, open to doubt whether this is a representative case or whether it does not more frequently happen that the atoms of the dissociated particles enter into combination in other ways. In the case of compounds which dissociate into their elements, the important question arises whether such are resolved into the isolated atoms, or whether the elementary atoms combine to form molecules. Mitscherlich[2] has shown, and his observation is confirmed by Victor and Carl Meyer,[3] that the density of the vapour of cinnabar at 669° is two-thirds that required by the formula HgS. Its

[1] See the numbers given by Naumann, *Thermochemie*, 1882, 155.

[2] *Pogg. Ann.* 1883, xxix. 225.

[3] *Ber. d. deut. chem. Ges.* 1879, xii. 1118.

decomposition is, consequently, represented by the following equation:—

$$2HgS = Hg + Hg + S_2.$$

This decomposition yields molecules, and not isolated atoms of sulphur.

This question might be decided experimentally in many cases, without great difficulty, were it not for the fact that dissociation takes place usually at temperatures so high that exact vapour density determinations are impossible. Whether, for instance, the dissociation of hydrogen chloride, pointed out by Deville, takes place in accordance with the first or second of the following equations, might without further data be determined from a knowledge of the density of the products of dissociation.

$$HCl = H + Cl$$

or

$$HCl + HCl = HH + ClCl.$$

For supposing the first of these equations to represent what takes place, then the density would only be half that of hydrogen chloride, whereas if the second equation be a correct interpretation of the facts, then the density will be the same as that of hydrogen chloride. All that is required, therefore, is to determine the density of the dissociated gases in comparison with that of undecomposed hydrogen chloride calculated for the same temperature; should a diminution in the density be observed then we have proof sufficient to show that at least a portion of the gas has been resolved into isolated atoms, the relative amount so decomposed may be calculated by the method already described.

The solution of the problem is simple only in the case of those compounds which are formed from their elements without change in volume, in other cases the solution is more complicated. For instance, to decide whether water is resolved into the atoms or molecules of its elements, thus:—

$$H_2O = H + H + O \qquad \text{or} \qquad 2H_2O = H_2 + H_2 + O_2$$

the dissociation must be carried so far that the density of the mixture is smaller than that of the mean of a mixture of two

volumes H_2, and one volume, O_2, for compared with air at the same temperature, the density of aqueous vapour is 0·62207, and that of its constituents resolved into their atoms would be 0·20736, whilst on the other hand it would be 0·41412 if these atoms had united to form elementary molecules. Supposing the density was found to be between 0·62 and 0·41, it might with equal justice be supposed to belong to a mixture—

$$(1 - x)H_2O + xH_2 + \tfrac{1}{2}xO_2$$

as to a mixture consisting of—

$$(1 - \tfrac{1}{4}x)H_2O + \tfrac{1}{2}xH + \tfrac{1}{4}xO$$

for in both cases one volume would expand $(1 + \frac{1}{2}x)$ volumes. So soon as the density sank below 0·414 then the only explanation which can be applied is that the elements have been resolved into atoms.

§ 208. Although suitable determinations of the vapour densities of dissociated compounds are wanting, still in many cases the properties of the elements themselves afford data for the solution of this question. From what has been stated in § 18 it will be seen that the molecules of the elements themselves are capable of dissociation; mercury, cadmium, and probably zinc, are resolved into atoms at once by conversion into vapour.

Sulphur is resolved at first into hexatomic molecules, and above 600° C. these become diatomic. Victor Meyer,[1] in conjunction with C. Meyer and H. Züblin, has shown that at temperatures above 600° C. the molecular weights of chlorine, bromine, and iodine are less than required by the molecular formulæ Cl_2, Br_2, and I_2. An observation confirmed by I. M. Crafts and F. Meier,[2] and although the results of these investigators show a smaller decrease in the density with rise in temperature, still both sets of observations show that even at the highest temperatures at which observations could be made the resolution into monatomic molecules at the pressure of

[1] *Ber. d. deut. chem. Ges.* 1879, xii. 1426; 1880, xiii. 394, 409, 1010, 1103, 1721, 2019; 1881, xiv. 1453.

[2] *Compt. Rend.* 1880, xc. 183, 309, 606, 690; 1881, xcii. 39. *Ber. d. deut. chem. Ges.* 1880, xiii. 851.

one atmosphere was never complete. The mean of the results of Crafts and Meier[1] gives the following data for iodine.

Temperature ° C.	Difference ° C.	Density D′	Difference	Per cent. decomposed 100 x.	Mean increase for 100° C.
445	—	8·76	—	0	0·9 per cent.
682	237	8·58	0·18	2·1	4·4 ,,
767	85	8·28	0·30	5·8	5·0 ,,
831	64	8·04	0·24	9·0	7·6 ,,
1043	212	7·01	1·03	25·0	11·0 ,,
1275	232	5·82	1·19	50·5	13·6 ,,
1390	115	5·27	0·55	66·2	8·6 ,,
1470	80	5·06	0·21	72·9	—

The dissociation is seen from these numbers to take place slowly; according to what has been said in § 205 the temperature of dissociation is 1270°, at which point the graphic representation of the observation shows a turning point in the density curve. Since the growth of the dissociation is symmetrical[2] on either side of the temperature of decomposition, the end will therefore be reached at a point as much above this temperature as the commencement is below, which consequently must be between 1800 and 1900° C. By a reduction of pressure the end of the dissociation may be reached more quickly. If the pressure of the vapour were reduced by the introduction of some indifferent gas, then the dissociation into monatomic molecules could be completed at a lower temperature.[3] From the fact that this resolution of the elements into free atoms has not been observed in the case of other elements, we cannot conclude that such a resolution is impossible. The high temperatures at which Deville has observed the dissociation of, in other respects, the most stable compounds, exclude the possibility of determining their vapour densities. From the analogy of other elements mentioned above we may regard it as very probable that at similarly

[1] *Ber. d. deut. chem. Ges.* 1880, xiii. 269 and 873; A. Naumann, *Thermochemie*, 1882, 119, etc.

[2] That the mean increase in this table for every 100° C. appears greater above 1270° than below it, is only an apparent contradiction, which may arise from the fact that the mean value, 11·0 per cent., represents an interval of temperature twice as great as that represented by the value 13·6 per cent.

[3] *Compt. Rend.* 1881, xcii. 39.

ıigh temperatures oxygen, nitrogen, hydrogen, &c., may at east partially be dissociated into atoms.

§ 209. On the other hand we are justified in concluding hat when a compound dissociates into its elements at a emperature below which the molecules of the elements would ›e further resolved, then the product of dissociation must ›nly contain elements in the condition of molecules and not ›f atoms. When, for instance, hydriodic acid, as observed by G. Lemoine,[1] is partially decomposed at 440° C. into hydrogen ınd iodine, then since the iodine molecule is not dissociated ›elow 600°, and only at very high temperatures, we may ›onclude with certainty that hydriodic acid is decomposed ıccording to the equation

$$HI + HI = HH + II,$$

ınd not as follows:

$$HI = H + I.$$

Accordingly, this cannot be considered as an instance of imple dissociation, but is either a case of dissociation, followed ›y recombination, thus:—

$$HI + HI = H + I + H + I = HH + II;$$

r simply an instance of chemical change,

$$\begin{array}{c|c} H & H \\ I & I \end{array} = \frac{HH}{II}$$

hich has but little in common with dissociation pure and imple. A more thorough consideration will, in fact, show hat many of the instances usually regarded as cases of dis›ciation may be in part or entirely explained as instances of ouble decomposition. For example, in the cases studied by Würtz of the decomposition of amyl iodide into amylene and ydriodic acid (*vide* § 33), and that of the corresponding ertiary alcohol into amylene and water, which can be repre›ented as follows:—

$$C_5H_{11}I = C_5H_{10} + HI$$
$$C_5H_{11}OH = C_5H_{10} + HOH.$$

t may be that the atoms H and I, or H and OH, are first

[1] *Ann. Chim. Phys.* [5] 1877, xii. 145.

liberated from their respective carbon atoms and then unite with one another, whilst the two carbon atoms combine with one another by double linking. Here also an exchange takes place; the question, however, may always arise, whether dissociation takes place first, to be followed by a re-combination, or whether the exchange takes place at once as a result of the attraction of the atoms. It may perhaps never be possible to separate completely the phenomena of dissociation pure and simple from cases of double decomposition, or to determine under what conditions one or the other of these takes place. This will probably remain impossible, because as a rule both occur simultaneously. We do not know whether the action of heat is to effect a complete dissociation followed by combination, or whether heat simply loosens the cohesion of the molecules in such a way as to afford the affinities the conditions necessary to effect the exchange. If, however, dissociation is to be limited to cases of decomposition pure and simple, then the majority of those phenomena now considered as cases of dissociation can no longer be regarded as such.

§ 210. The phenomena, long regarded as inexplicable, that many substances decomposed by moderate heat are reproduced when the products of dissociation are strongly heated and then suddenly cooled, may probably be explained as cases of simple dissociation, followed by a chemical exchange taking place after cooling. Ammonium cyanide, for instance, according to Deville and Troost,[1] gives a vapour which has a density of 0·79 at 100° C., whilst a mixture of hydrocyanic acid and ammonia would have a density of 0·76. Both substances unite on cooling to form ammonium cyanide. At a dull red heat, however, hydrocyanic acid begins to decompose into cyanogen and hydrogen, thus:—

$$HCN + HCN = CN + CN + HH,$$

and above 1000° C. ammonia is also partially resolved into nitrogen and hydrogen. Ammonium cyanide is nevertheless formed at a white heat from carbon and ammonia, or rather, the latter is dissociated at this heat from carbon, hydrogen, and nitrogen. This can only be explained by supposing that

[1] *Compt. Rend.* 1863, lvi. 253; *Ann. Chim. Phys.* 1863, cxxvii. 282.

the products of decomposition at a moderately high temperature, which on cooling do not recombine to form ammonium cyanide, are at a red heat resolved into free atoms, which on cooling combine to form together with other substances ammonium cyanide. Similar phenomena have frequently been observed.

§ 211. Bearing in mind that heat accelerates chemical action, its influence on the phenomena of dissociation can be easily explained.

Increased acceleration of the motion of the atoms by heat increases the distance which the atoms are removed from their position of equilibrium, and consequently exposes them to a greater extent to the action of external influences, such as the attractive force of the atoms of other molecules. A further corroboration of this is found in the fact that many chemical changes do not take place below certain temperatures. Even those substances which unite to form very stable compounds, and may therefore be supposed to have strong affinity for one another, often require to be strongly heated to induce chemical union. Hydrogen and oxygen, for instance, may be allowed to stand in contact with one another for any length of time without producing the smallest quantity of water, nor do they unite until they have been heated to redness. The atoms, despite the innumerable impacts of the molecules, never appear to come into such a position that the affinity of hydrogen for oxygen is able to effect a combination. This may either arise from the fact that the molecules never approach one another so nearly as to allow the force of affinity, which only acts at short distances, to come into play, or it may be that at low temperatures the atoms in the molecules are so close together that the affinity of hydrogen for hydrogen, and of oxygen for oxygen is so strong as not to be overcome by that of the hydrogen for the oxygen. The latter explanation depends upon the assumption that at small distances the affinity of like atoms for one another is the stronger, whereas at greater distances that between unlike atoms is the more powerful. From this point of view, however, it is not evident why at ordinary temperatures the particles of water do not decompose into hydrogen and oxygen,

and hence the first supposition would appear the more probable. But this hypothesis has not up to the present explained what it is that interferes with the approximation of the atoms in spite of these constant impacts. Since observation teaches us that at least the majority of chemical changes require for their commencement the attainment of a definite temperature, so it is probable that for each a certain lower limit of temperature exists, below which the change does not take place. And since at the lowest temperature to which we can attain, the majority of chemical reactions studied under these conditions have been found to cease entirely or to proceed very slowly, so it would appear to be very probable that at the absolute zero, viz. $-273°$, a temperature much below the lowest yet attained, chemical action would altogether cease, from the absence of any form of heat motion whatsoever. So without heat there would be no exertion of the so-called affinity, and for the reason that under these conditions all substances would be solid and none liquid or gaseous.

§ 212. The lowest temperature at which chemical action takes place between combustible bodies is styled the temperature of ignition; it varies considerably, depending as it does upon the nature of the substances and their physical condition. It often happens that those very elements, which form the most stable and most difficultly decomposible compounds, to which consequently we attribute the strongest affinities, are those requiring the highest temperature to bring into play their active powers; examples of this character are afforded by oxygen, carbon, nitrogen, and many metals. On the other hand, it is often the case that those elements, which react at low temperatures, form easily decomposible compounds. Chlorine and sulphur unite even at 90° C., but their compounds with one another are very unstable; whilst those of oxygen and sulphur are more stable, but are not formed at temperatures below 250° C. Carbon does not combine directly with chlorine under any circumstances, yet the majority of the compounds of these two elements are decomposed with difficulty. These and innumerable similar differences depend apparently on the elements not existing as free atoms, but only as molecules, the coherence of which must be sufficiently loosened before the

atoms can pass over into other compounds. The stronger the affinities, so much the higher will be the temperature required to initiate their action. That carbon usually reacts only at very high temperatures is easily understood, when we remember that it is this very element which, as shown by the numerous organic compounds, is distinguished by the special tendency, which its atoms exhibit, to unite with one another. The indifference of free nitrogen at low temperatures is also doubtless to be explained by the strong affinity of its atoms for one another, resisting as it does the resolution of the molecule into atoms.

What has been said of the elements applies equally to their compounds. The temperature required to start their action depends not merely on the nature of the atoms, which unite to form the compounds resulting from the change, but rather upon the nature of those whose union must be dissolved in order that the action may take place. Every chemical change is the result of the simultaneous action of heat, producing dissociation, and of affinity, *i.e.* the tendency of the atoms to unite with one another.

§ 213. Since heat prepares the way for affinity, it, as a rule, ceases entirely or in part to be heat, inasmuch as it is changed into other forms of kinetic or potential energy, no longer perceptible as heat, and therefore effects changes in the condition of disgregation of the substances. On the other hand affinity may be converted into heat; it may be, that by the union of the atoms motion is produced and therefore the existing potential energy is converted into kinetic, or that certain motions of the atoms, not perceptible as heat, are converted into it, and therefore one form of kinetic energy passes into another. Inasmuch as affinity, be its nature what it may, is subject to the law of the equivalency of the different forms of energy, so the heat produced in a chemical change affords a means of measuring the change of energy accompanying the action.

Starting with the hypothesis that unsaturated affinities represent potential energy, then the heat produced by a chemical change is a measure of the forces to which this potential energy belongs, and therefore of the attraction of the

atoms. The use of this means of estimating these forces is, at all events, associated with considerable difficulties. If it were demonstrated that affinity is a species of attraction, and we could follow the motions of the atoms under its influence, just as we observe the movement of a falling body or the course of the heavenly bodies in obedience to the force of gravity; or if it were possible to determine the acceleration imparted to the atoms, for all distances, then the law of affinity would be as evident to us as the laws of gravity, and of the general attraction of mass. But, as is well known, the matter is by no means so simple. 'Ad opera nil aliud potest homo quam ut corpora naturalia admoveat et amoveat; reliqua natura intus transigit.'[1] No special difficulties arise from the fact that we cannot investigate the atoms themselves, because our knowledge of the stochiometric laws enables us to make use of masses proportional to the atoms, the action of which must be proportional to that of the single atoms. The difficulty lies rather in the fact, that we possess no knowledge whatever of the true existence of the combination and separation of the atoms. Lacking this knowledge we cannot determine in what way distance of separation affects the attraction of the atoms, nor how the velocity and consequently the momentum increases with the mutual approximation of the atoms. We may at the most be able to measure the sum of the total momentum developed, whilst the atoms approach one another from a distance at which no commensurate action takes place, to one of greatest possible proximity. This is comparable with the momentum or kinetic energy which would be imparted to a body falling to the earth from a very great or infinite distance. It is impossible to take in hand measurements of chemical affinity, which would be analogous to the experiments made with an Atwood's machine, from which the velocity of a body at any moment and any hour may be deduced.

We know that the chemical forces are exceedingly small even at distances so minute as to be almost incapable of measurement, and that they become extremely powerful at still more minute distances, that, therefore, they increase rapidly

[1] Bacon, *Novum Organum*, Lib. 1, Aphor. IV.

with decreasing distance, and probably much more rapidly than gravity for instance, which is always proportional to the inverse of the square of the distance between the active masses. But as we do not know whether the law, in accordance with which the attraction of the atoms increases with the diminution of the distance, is the same for all substances, so we are unable to say whether, in the case of two atoms which by complete approximation attain a greater momentum and consequently produce more heat than two others, under all conditions the former would attract each other more powerfully than the latter. It is not impossible that, when at a given distance the attraction of A to B is greater than that of B to C, the latter may increase as the distance between them becomes less, and hence at a smaller distance the attraction may not only be greater than that between the other two, but also produce on the whole a greater total momentum. Although the possibility of this being the case has not been proved, still it should be held in remembrance, as it may perhaps serve to give the clue to the explanation of phenomena otherwise inexplicable.

§ 214. It is further evident that, as already mentioned in Chapter X., the complex nature of almost all chemical phenomena brought within the range of observation renders their exact investigation excessively difficult, more especially the measurement of the individual forces taking part in them. Such measurements would require, what has hitherto remained impossible, viz. the exact calorimetric investigation either of the pure syntheses of compounds, that is to say, their production from the isolated atoms, or of their decomposition into these ultimate parts.

At all events, it can no longer be doubted that all elementary bodies may be resolved into free atoms; but, hitherto, we have only succeeded in doing so for a small number, *e.g.* zinc, cadmium, mercury, chlorine, bromine, and iodine, and even in these cases, which, with the means at our command, are the most easily attainable, such high temperatures have been required as almost to exclude the possibility of exact calorimetric measurements, and under conditions which render the combinations of atoms with others impossible.

It is, therefore, impossible for us at the present time to state in the case of the different chemical compounds, what is the total expenditure of potential energy (affinity), which in production of them from free atoms is converted into kinetic energy (heat). The production of a compound from others or from the molecules of its constituents can only serve to give a complete account of the affinities active in its production, when we know how and in what way the compounds used in its production are held together. For when we prepare chemical compounds from other already existing compounds of atoms, then it is necessary, as already mentioned in § 189, that in all cases the affinities must be overcome and liberated, before other different states of combination can be entered upon. Since this in itself requires a certain expenditure of work, therefore the potential energy of the affinities cannot be completely converted into kinetic energy or heat, but only the portion in excess of that used up in the manner described.

For example, if hydrogen is burnt with chlorine in a space kept at the ordinary temperature, such as the interior of a calorimeter, then, according to Thomsen,[1] for every unit weight of hydrogen, and therefore for 1 atom, 22000 calories or thermal units are produced; or an amount of heat, which would suffice to raise through 1° C. 22000 times the weight of the burnt atom or 22000 parts by weight of water. This amount of heat is not the measure of the affinity of one atom of hydrogen for one atom of chlorine, but is equivalent to the potential energy of this affinity minus the work expended in the separation of the atoms in the molecules of the elements from one another. Since the change takes place according to the equation,

$$HH + ClCl = HCl + HCl,$$

then the kinetic energy produced thereby is represented by the equation,

$$(H_2 : Cl_2) = 2(H,Cl) - (H,H) - (Cl,Cl) = 44000 \text{ cal.},$$

[1] *Ber. d. deut. chem. Ges.* 1871, iv. 942. Since Thomsen takes O = 16 in his investigations, then the number used above represents really the heat produced by the union of 1·0025 parts by weight of hydrogen with 35·46 parts by weight of chlorine. One part by weight of hydrogen produces 21950 thermal units.

n which, according to the nomenclature introduced by Thomsen,[1] each bracket represents the heat produced or calorific effect (abbreviated into c. e.) which is produced from the compound of the quantities surrounded by the brackets and separated by a comma. This c. e. is regarded as positive when heat is produced, *i.e.* when potential is converted into kinetic energy, and negative when the opposite takes place. The above equation indicates that the experimental determination of the total c.e. does not suffice to determine the affinity between H and Cl, *i.e.* the value (H,Cl). We may, however, eliminate any other of these quantities occurring in this equation, *e.g.* (H,H), by the investigation of any other reaction in which they occur. Thus, this quantity is contained in the following equation—

$$(H_2 : Br_2) = 2(H,Br) - (H,H) - (Br,Br) = 16880 \text{ (cal.)}.$$

But every new reaction introduces usually at least one other unknown value, so that we have more unknowns than equations required for their determination. Consequently, the measurement of heat produced by chemical action cannot suffice to give an absolute measure of the affinities. With the means at present at our disposal we can only measure the difference between several affinities. Thus from the above examples we can only conclude that the potential energy of the affinity of chlorine for chlorine is greater by the above-mentioned quantity than that of the affinity of hydrogen for hydrogen. The absolute value of these different affinities remains, however, in our present state of knowledge, unknown to us.

§ 215. A number of equations corresponding to the total number of values to be determined can only be obtained on a hypothesis, hitherto unverified, viz. that the several units of affinity of a polyvalent atom are equal, and that the same quantity of heat is always produced by their combination with one and the same element. If, for instance, the calorific effect of the formation of gaseous mercurous chloride and mercuric chloride from their gaseous constituents were known,

[1] 'Grundzüge eines thermochemischen Systemes,' *Pogg. Ann.* 1833, lxxxviii. 349, §§ 4 and 5, *v.* also *Thermochemische Untersuchungen*, i. 1882, 4.

then, since the molecule of mercury is monatomic, we should have the following—

$$\tfrac{1}{2}(2Hg : Cl_2) = (Hg,Cl) \quad -\tfrac{1}{2}(Cl,Cl) = A$$
$$\tfrac{1}{2}(2HgCl : Cl_2) = (HgCl,Cl) - \tfrac{1}{2}(Cl,Cl) = B.$$

Although two equations are given here for two values still we cannot determine them, since, supposing the hypothesis that both the units of affinity of the mercury atoms are equal to be correct, then A must be equal to B. If this is not the case, then the c. e. of (Hg,Cl) must differ from that of (Hg_2Cl,Cl), and so we have again three unknowns. It is also obvious that all equations of this character contain not only the action of each chlorine atom, but also the member $-\frac{1}{2}$(Cl,Cl), *i.e.* a quantity representing half the expenditure of work necessary to the separation of a molecule of chlorine, and therefore these quantities cannot be separated by any process of elimination. In a like manner, in the case of the oxidising action of oxygen the quantity $\frac{1}{2}$(O,O), or in the case of combination of hydrogen the quantity $\frac{1}{2}$(H,H), cannot be eliminated from the c. e.

But by regarding the sum of such conjugated quantities as the unknown quantities to be determined, then the problem is to some extent simplified, and by the aid of suitable hypotheses a tolerably complete solution can be obtained. In this manner Julius Thomsen [1] has recently instituted calculations for the compounds of carbon, from which conclusions have been drawn as to their atomic linking.

By supposing that both the oxygen atoms contained in carbonic anhydride, CO_2, in combining with an isolated carbon atom do so with the production of an equal c. e., he has calculated from the heat of combustion of solid carbon (charcoal) and of carbonic oxide the expenditure of work, *d*, necessary to set free an atom of solid carbon and convert it into the gaseous state. When carbon and carbon monoxide burn we obtain the following—

$$(C,OO) - d - (O,O) = 96960 \text{ c.}$$
$$(CO,O) \quad -\tfrac{1}{2}(O,O) = 68080 \text{ c.}^{2}$$

[1] *Ber. d. deut. chem. Ges.* 1880, 1321, 1388, 1806, 2166.

[2] Or 67960 c., *vide Therm. Untersuch.* I. 289.

'rom which it follows that the heat of combustion when on burns to carbon monoxide is—

$$(C,O)-d-\tfrac{1}{2}(O,O) = 96960-68080 = 28880^{c.}$$

w

$$(C,O) = (CO,O) = \tfrac{1}{2}(C,O,O),$$

nomsen's hypothesis assumes, then the heat of disgrega- for 1° C. is—

$$d = 68080-28880 = 39200^{c.}$$

the aid of this value Thomsen then calculates further alue (q),

$$q = (C,H)-\tfrac{1}{2}(H,H) = 14687^{c.},$$

also the c. e. produced by the combination of isolated on atoms with one another, and finds the remarkable lt to obtain, that by the union of each single affinity with another the same c. e. is produced as by the union of a le atom of hydrogen (*i.e.* q).

$$(\equiv C-,-C\equiv) = 14805^{c.},$$

an amount which is scarcely greater in the case of union wo affinities—

$$(=C=,=C=) = 15033^{c.},$$

n the case of union by three affinities it becomes almost finitely small, viz.—

$$(-C\equiv,\equiv C-) = 688^{c.}$$

These great differences have enabled him to arrive at the lusions already mentioned in § 143 regarding the atom ng in different hydrocarbons, amongst others that of ene, which promise to become important aids to our vledge of organic compounds.

These calculations show, independently of the truth of the thesis upon which they rest, that what we style double triple union of the atoms does not consist of a simple dition of that which we regard as simple union. Since no ons can be assigned for supposing a difference amongst all four affinities of the carbon atom (and if such existed it d not help us in this case), we can only, therefore, explain

this remarkable result as indicating that two carbon atoms, which are already united by one affinity, have thereby lost the ability to unite again in a similar manner with one or two of their affinities.

Moreover, these investigations show that the calorific effect

$$q = (C,H) - \tfrac{1}{2}(H,H)$$

cannot be deduced, as one might have previously expected, solely from the addition of hydrogen to an unsaturated hydrocarbon, since hydrogen will give rise to a different c. e., according as it unites with carbon atoms either uncombined or combined with another, and this again according as the combination is effected by one, two, or three combining units.

Starting with the hypothesis that the band spectrum produced in gases by the electrical discharge changes into a line spectrum in consequence of a resolution of the molecules into atoms, Eilhard Wiedemann [1] concludes that to effect this change in the case of hydrogen, 128,000 heat units would be necessary for every unit weight of hydrogen. This heat serves in part to raise it from the ordinary temperature and also to effect the resolution of its molecules into atoms. Granting this hypothesis to be correct, then we may consider the following to be a fair approximation—

$$\tfrac{1}{2}(H,H) = 120000^{c.}$$

and consequently,

$$\tfrac{1}{2}(C,H) = 135000^{c.}$$

Wiedemann's observations show that the heat required for the dissociation of the nitrogen molecule would be considerably greater; a result which the properties of nitrogen would lead one to expect.

It is nevertheless remarkable that the heat of disgregation of hydrogen, as estimated by Wiedemann, is nearly three times as great as that required, according to Thomsen, to effect a similar change in solid carbon, which is entirely opposed to our knowledge of this substance. This fact shows the necessity for a careful examination of the hypotheses upon which these calculations are based.

[1] *Wied. Ann.* 1880, x. 233, 252; 1883, xviii. 509.

§ 216. That the calorific effect accompanying the production of a compound is not alone produced by the action of the combining affinities, but is influenced specially by the expenditure of work necessary to the release of previously combined affinities, is shown by the fact that the production of several compounds is attended by a negative calorific effect, *i.e.* an absorption of heat. Thus, for example, according to J. Thomsen,[1] the formation of hydriodic acid from hydrogen and iodine is accompanied by a negative c. e. $= -6036$ c., and consequently the decomposition of the compound will be accompanied by an equal but positive c. e. If we suppose the formation and decomposition to take place according to the equations—

$$H + I = HI \text{ and } HI = H + I,$$

then it follows that (H,I) must be $= -6036$ c. That is, the production of the compound results from movements opposed to the affinities, whilst the decomposition takes place in accordance with such movements; or, in other words, iodine and hydrogen have no attraction for one another, but rather repel one another. It would then be entirely inexplicable why these elements should combine at all, and the compound once formed should decompose immediately into its elements. This apparent contradiction disappears at once, if we suppose both these phenomena to be more accurately represented by the following equations—

$$HH + II = HI + HI$$
$$HI + HI = HH + II,$$

and in consequence the calorific effects by the following—

$$\tfrac{1}{2}(H_2 : I_2) = (H,I) - \tfrac{1}{2}(H,H) - \tfrac{1}{2}(I,I) = -6036 \text{ c.}$$
$$\tfrac{1}{2}(HI : HI) = \tfrac{1}{2}(H,H) + \tfrac{1}{2}(I,I) - (H,I) = +6036 \text{ c.}$$

It is at once evident that all the three quantities (H,H), (I,I), and (H,I) must be positive; without invalidating these equations, each of the atoms can have an affinity, and in fact a very great affinity, for similar as well as for dissimilar atoms. The observation that—

$$(H,I) + 6036 \text{ c.} = \tfrac{1}{2}(H,H) + \tfrac{1}{2}(I,I)$$

[1] *Ber. d. deut. chem. Ges.* 1872, v. 770.

indicates only that the affinity of iodine for hydrogen is smaller, by 6036 heat units, than the sum of the affinities by which the atoms of each of the elements is attracted by its like. Since these latter are, according to the investigations mentioned in the foregoing, very powerful forces, so also are the former; but the difference of 6036 c. is small compared to the heat required, according to Wiedemann, to dissociate the molecule of hydrogen.

§ 217. Nevertheless our knowledge, although so limited, is of great value in determining the comparative affinities of different elements, since it allows us to determine by how much the affinity of one element for another is greater than that of a third element for this latter. Thus, for instance, we know from the observations of J. Thomsen [1] that—

$$\tfrac{1}{2}(H_2 : Cl_2) = (H,Cl) - \tfrac{1}{2}(H,H) - \tfrac{1}{2}(Cl,Cl) = 22000 \text{ c.}$$
$$\tfrac{1}{2}(H_2 : Br_2) = (H,Br) - \tfrac{1}{2}(H,H) - \tfrac{1}{2}(Br,Br) = 8440$$
$$\tfrac{1}{2}(H_2 : I_2) = (H,I) - \tfrac{1}{2}(H,H) - \tfrac{1}{2}(I,I) = -6036.$$

These results do not prove that the affinity of chlorine for hydrogen is greater than that of bromine, and this than that of iodine; for these equations indicate only that—

$$2(H,Cl) - 2(H,Br) - (Cl,Cl) + (Br,Br) = 27120 \text{ c.}$$
$$2(H,Br) - 2(H,I) - (Br,Br) + (I,I) = 28952;$$

or that

$$2(H,Cl) + (Br,Br) = 2(H,Br) + (Cl,Cl) + 27120 \text{ c.}$$
$$2(H,Br) + (I,I) = 2(H,I) + (Br,Br) + 28952.$$

But, as the affinities (Cl,Cl), (Br,Br), and (I,I) are unknown, we cannot say whether the sum of the calorific effects on the left-hand side in the above equation is greater than those on the right-hand side, because—

$$(H,Cl) > (H,Br) > (H,I),$$

or because

$$(Cl,Cl) < (Br,Br) < (I,I).$$

Bearing in remembrance the facts that in numerous instances hydriodic acid is more easily decomposed than hydrobromic

[1] *Ber. d. deut. chem. Ges.*, 1871, iv. 942; 1872, v. 770. *Therm. Unters.* 1882, ii. 37. The numbers given are those for gaseous chlorine, liquid bromine, and solid iodine.

acid, and this latter than hydrochloric acid, and that the molecules of the halogen elements offer as a rule but little resistance to their decomposition, then it appears in the highest degree probable that the affinity of chlorine for hydrogen is considerably greater than that of bromine, and this latter than that of iodine. How great the difference of energy of these three affinities is cannot be definitely stated, as long as the quantity of work necessary for the resolution of the molecules of these elements remains unknown to us.

§ 218. Investigation becomes much more difficult than in these relatively simple cases, and the conclusions more uncertain, when a large number of quantities representing affinities come into play. Then indirect methods have often to be employed in order to separate as far as possible the individual calorific effects and to determine their amount. Investigation depends, in this case, upon that law of the mechanical theory of heat which states that when one system of mass passes from one condition to another, without giving out energy or receiving any from without; the change thereby produced in the energy of the system is dependent only upon the primal and final conditions, not upon the manner in which the change takes place nor upon the different stages through which it passes.

When, for instance, carbon burns in oxygen to form carbon dioxide, then as far as the heat produced is concerned, *i.e.* the change from potential to kinetic energy, it is a matter of indifference whether carbon dioxide be the immediate result or carbon monoxide, which is further completely burnt. In the same way the calorific effect accompanying the formation of carbon monoxide is one and the same, whether it be produced directly from carbon and oxygen, or whether carbon dioxide be first formed, which afterwards by an expenditure of energy is reduced to carbon monoxide.

By the aid of the same law calorific effects may be determined indirectly in cases where direct determination is impossible. Thus, for example, the combustion of carbon to carbon monoxide cannot be so conducted as to allow of calorimetric determinations. Observation, however, shows that one atom of carbon (as charcoal), or, in round numbers,

12 parts by weight, burning to carbon dioxide, give 96,960 units of heat or calories, whilst the quantity of carbon monoxide represented by the formula CO, 28 parts by weight and also containing one atom of C, on burning to form carbon dioxide gives 68,080 heat units. Since according to the above law the same quantity of heat is produced, whether carbon monoxide be first produced or not, then the difference between 96,960 and 68,080, viz. 28,880, must represent the calorific effect attendant on the conversion of C into CO.

In fact, it is often a matter of necessity to deduce the calorific effect of a reaction from the one equivalent to it, but of the reverse order, as, for instance, in the determination of the amount of heat required to decompose water from that liberated in its formation.

§ 219. Many chemical decompositions are not suited to calorimetric measurement, because they take place either too slowly or incompletely, or under conditions otherwise unsuitable, because they are not capable of direct performance or only in a very circuitous manner. Such reactions may, however, be investigated calorimetrically by the aid of the above cited law of the mechanical theory of heat, if the calorific effects can be measured which are associated with the passage from the primal and final states into any particular third condition—the difference in these calorific effects representing that which would suffice to produce the direct passage from the primal to the final state.

Supposing the question to arise, What is the calorific effect accompanying the formation of the molecule of marsh gas, CH_4, from one atom of carbon as charcoal and four atoms of hydrogen in the gaseous state? We have here a change which we cannot produce directly. But if we imagine the carbon to be burnt to carbon dioxide and the hydrogen to water, then, as far as concerns the quantity of heat produced, it is of no importance in what manner the change takes place. Supposing the carbon and hydrogen be first allowed to combine to form marsh gas, and then this compound to be burnt to form carbon dioxide and water, according to § 218, the sum of the amounts of heat produced in these changes must be exactly the same as that produced by the immediate com-

bustion, for the primal and final states are the same. We have, therefore—

$$(C,O_2) + (2H_2,O_2) = (C,2H_2) + (CH_4,2O_2),^1$$

and therefore the heat of formation of marsh gas is—

$$(C,2H_2) = (C,O_2) + (2H_2,O_2) - (CH_4,2O_2).$$

That is, the heat of formation of marsh gas when formed from carbon and hydrogen is equal to the heat of combustion of the isolated elements minus that of marsh gas itself.

In this indirect manner a number of calorific effects have been determined. It is frequently necessary to make determinations in a large number of instances, in order to deduce the desired quantity from the sums or differences of their calorific effects. Naturally the uncertainty of the determination increases with the number of measurements, since the final result will be influenced by the accumulated errors of experiment.

§ 220. Another considerable difficulty surrounds such observations, arising from the fact that frequently the calorific effect of a chemical change is accompanied by others which are sometimes positive, sometimes negative, produced by changes of state resulting from the chemical changes; hence the total calorific effect differs from that which is the immediate result of the chemical change, and represents the true action of affinity.

These physical calorimetric actions accompanying those which are chemical in origin are to be attributed to the fact that all the conditions within the range of our observation are conditions of matter in motion, and, therefore, always containing kinetic energy, the quantity of which varies with the conditions, the amounts of the changes in which we are unable to measure in every case. It is also possible that there may be not only kinetic and potential, but other forms of energy to deal with, which are likewise subject to change and distinct from true affinity, *i.e.* the attraction of the atoms. The heat produced by a chemical change cannot

[1] In both cases the quantities of heat necessary for the decomposition of the molecules of O_2 and H_2 have been left out of consideration, for the sake of simplicity.

be taken as a measure of the saturated affinities, unless, after removal, the kinetic, together with the potential energy present (which cannot be regarded as affinity) remaining in the system of the mass, is exactly as great as that present before the chemical change took place. But this, perhaps, is never found to be strictly the case, seldom approximately so, and in many cases this condition never obtains. Numerous chemical changes are more frequently found to be associated with very considerable changes of physical condition, of density, of state of aggregation, of crystalline form, of specific heat, &c., which Clausius has classed together under the name of 'disgregation'[1] or degree of separation. Every increase in the dissolution or disgregation requires work, or an equivalent amount of heat, which is derived from the amount already present or from the quantity produced by the chemical change; on the other hand, every diminution of the disgregation produces heat, and the calorific effect of the chemical process is thereby raised.

When, for example, gases unite to form solid bodies, their disgregation is diminished, and an amount of heat corresponding to this diminution is produced or liberated, as we say —an expression not altogether suitable, but the one most in accordance with present views. If gases, on the other hand, are formed from solid or liquid bodies, or liquids from solids, then heat is used up, and the calorific effect diminished to supply the same. Considerable changes of disgregation may arise without changes of state. In the combination of gases accompanied by contraction the kinetic energy of the accelerated motion of the reduced volume is converted into heat, although, for instance, chlorine and hydrogen combine without contraction. Still the calorific effect of this combination is not to be attributed to affinity alone, for the specific heat of the compound is more than 12 % less than that of the constituents; the difference in both produces, therefore, an increase of the calorific effect. Consequently the action of affinity appears greater than it really is. Similar phenomena accompany almost every chemical change, and influence the calorific effect of the same, in some cases to a greater, in others to a smaller extent.

[1] Compare § 40.

§ 221. In order to determine the relation of the calorific effect to chemical affinity, it is necessary to separate it from all actions resulting from changes in disgregation. Since these, as a rule, are unavoidable in our experiments, then their thermic effect must be determined and subtracted from the total heat produced. It is theoretically possible to do this, but, at the present time, in a small number of cases only can it be completely carried out, inasmuch as many of the changes of disgregation are still completely beyond determination. But even in the few cases within reach, the investigators who have studied these phenomena are not agreed as yet on the method of calculation. This in part arises from the difficulty of the subject itself, but principally from the fact that so long as the great majority of thermochemical investigations have no bearing on cases of the real action of affinity, little attention has been paid to the methods of calculation in the few cases in which the thermochemical research deals with the action of affinity pure and simple.

In the majority of cases investigators have satisfied themselves with determining the calorific effects, including the actions of dissociation, and have only mentioned the state of the bodies investigated before and after the change, without which statement the calorimetric determinations would naturally be valueless. Up to the present it has only been possible to calculate with anything like accuracy the changes of disgregation in the case of gases, and this has been done in the manner illustrated by the following example.

If hydrogen be burnt with oxygen (in a space kept at the ordinary temperature—for instance, in the interior of a calorimeter) under the pressure of one atmosphere, forming water, then, according to J. Thomsen,[1] every unit weight of hydrogen produces 34,100 calories, an amount of heat by which 34,100 units of weight of water can be raised by 1° C.[2] This amount of heat is not to be attributed to affinity alone, but in part to the kinetic energy which the two gases contained, in excess of that contained by the liquid produced from their combination.

[1] *Ber. d. deut. chem. Ges.* 1871, iv. 944.

[2] If O is taken as 16, and H equal 1·0025, as Thomsen usually does, the number for one atom H is 34188 c.

At first from two molecules of hydrogen and a molecule of oxygen, two molecules of steam are produced—

$$HH + OO + HH = HOH + HOH.$$

Since, at the same temperature, two particles of steam possess a smaller kinetic energy than the three gaseous particles from which they have been produced, or, what amounts to the same, will with equal kinetic energy indicate a higher temperature, then the excess above this will be given out as heat to the surrounding bodies. By cooling, however, the steam is converted into water, losing, at the same time, the whole kinetic energy depending on its gaseous condition, or the so-called latent heat of vapour.

Both losses raise the temperature of the calorimeter, and make the true heat of combustion appear too great; and must, therefore, be deducted from this amount. This has been attempted in different ways. A. Naumann[1] deducts the kinetic energy of the rectilinear motion of the volume of gas disappearing in the act of combination, which has at the same temperature the same value for the molecular weight of all gases.[2] According to § 14 and § 16, this value for air, and therefore for every other gas, is—

$$\frac{\mathfrak{M} \cdot u^2}{2} = \frac{28{\cdot}87}{2} (485^m)^2 \cdot \frac{T}{273} = 3395000 \cdot \frac{T}{273}.$$

Since the mechanical equivalent of the unit of heat amounts to 425^m, and when g represents the acceleration of gravity, then—

$$1^{cal} = 425^m \cdot g = 425^m \cdot 9^m \cdot 806 = 4168q^m,$$

hence it follows that the rectilineal motion of the molecular weight of any gas at the absolute temperature T is equivalent to the following value—

$$K = \frac{3395000}{4168} \cdot \frac{T}{273} = 2{\cdot}99\,T;$$

or, roughly, $= 3T$; that is, for every degree of temperature it is equivalent to three heat units.

[1] *Annalen*, Suppl.-Bd. vi. 295; Gmelin Kraut, *Handb. der anorg. Chemie*, I. i. 284.

[2] Compare § 15.

Then, since for every two molecular weights, or four parts by weight of hydrogen, one molecular weight of oxygen is taken up, then in the burning of one part by weight of hydrogen the diminution of the kinetic energy of the rectilinear motion—

$$= \frac{3}{4} T;$$

or, if the experiment is made at 20° C.—

$$= \frac{3}{4} 293. = 220^{c.};$$

and in the burning of a molecular weight, or two parts by weight—

$$\frac{3}{2} T = 440^{c.}$$

J. Thomsen arrives at the influence of contraction in a somewhat different manner.[1]

If a gas under the pressure p expands by the volume v, then it has to do external work amounting to $p.v$.

When it is compressed under the same pressure to a similar volume, an amount of heat equivalent to the above will be liberated. But, according to the kinetic theory of gases (see § 14)—

$$p.v = \frac{1}{3} . n \mathfrak{M}u^2;$$

or, for the volume containing one molecular weight—

$$p = \frac{1}{3} \mathfrak{M}u^2 = \frac{2}{3} . \frac{\mathfrak{M}u^2}{2}.$$

Consequently, the expenditure of work is only two-thirds as great as that resulting in the former calculation: therefore = 2 T, or is equivalent to two-thirds of the kinetic energy of the rectilineal motion. This correction of Thomsen's is therefore a third smaller than that proposed by Naumann. But neither represents quite correctly the loss in kinetic energy, to which the uniting bodies are subject; for, as the motion of the molecules changes, so also does that of their constituent

[1] *Ber. d. deut. chem. Ges.* 1880, xiii. 1326.

atoms. According to Clausius,[1] the whole of the kinetic energy of a gas is related to the rectilineal motion of its molecules, in the manner expressed by the following formula—

$$\frac{H}{K} = \frac{2}{3}\left(\frac{c}{c'-c}\right);$$

in which c' represents the specific heat under constant pressure, and c that of constant volume. Hence we have for the molecular weight of any gas—

$$H = \frac{2}{3}\left(\frac{c}{c'-c}\right) . 3T = 2 . \frac{c}{c'-c} . T.$$

But for hydrogen and oxygen it is—

$$\frac{c'}{c} = 1{\cdot}410; \text{ therefore, } \frac{c}{c'-c} = \frac{1}{\frac{c'}{c} - 1} = 2{\cdot}439.$$

consequently—

$$H = 4{\cdot}88\ T.$$

Therefore each of these gases contains, in its molecular weight, at every degree of absolute temperature, 4·88 heat units as its total heat motion, 3 of which are to be attributed to the rectilineal motion, 1·88 to the motion of the atoms within the molecules.

According to Clausius,[2] the values for steam are—

$$c' = 0{\cdot}4750, \quad c = 0{\cdot}3637, \quad \frac{c'}{c} = 1{\cdot}306.$$

Consequently the total kinetic energy of the molecule is—

$$H = \frac{2 . T}{0{,}306} = 6{\cdot}536 . T,$$

and that of the motion of the atoms in the molecule—

$$H - K = 3{\cdot}536 . T,$$

according to which, if the steam produced were cooled to 100° C. it would then contain in the molecular weight the total kinetic energy—

$$H = 6{\cdot}536 \times 373 = 2438\ ^{c},$$

[1] *Abhandlungen über die mechanische Wärmetheorie*, 1. Aufl. ii., Abh. xiv. 258 (*Pogg. Ann.* c.).

[2] Liebig's *Annalen*, 1861, cxviii. 118.

whilst the other half of the molecular weight of the gas, from which the water was produced, contained before combustion at 20° C. only—

$$H = \frac{3}{2} \times 4{\cdot}88 \times 293 = 2245^{c.}$$

therefore 193 c. less.

If the steam condensed to form water having the temperature of 100° C., then for every unit of weight there will be liberated 536·5 c. for the molecular weight, therefore—

$$536{\cdot}5 + H_2O = 536{\cdot}5 \times 17{\cdot}96 = 9638^{c.}$$

and further, in the cooling of the water to 20° C., there will be liberated—

$$17{\cdot}96 \times 80 = 1437^{c.}$$

Therefore, from the amount of heat produced as determined by the calorimeter, for every molecular weight a deduction must be made amounting to the following—

$$9638 + 1437 - 193 = 10880^{c.};$$

consequently, for every molecular weight of hydrogen burnt the number of calories to be ascribed to affinity will be obtained by subtracting the above number from the total heat produced, thus—

$$2 \times 34100 - 10880 = 57320^{c.}$$[1]

Corrections of this character cannot at present be accepted without reserve, as the views upon which they depend have not been proved to be quite unimpeachable. The values taken as representing the specific heats at constant volume are by no means trustworthy.

The determination of the amount of disgregation and the calorific effects associated with it is, in the case of liquids and solids, still more difficult than in the case of gases. Indeed scarcely any real attempts have been made to separate the calorific effects depending on affinity from those accompanying it and dependent upon changes in disgregation. In many

[1] There is little difference between this number and that obtained by employing Naumann's or Thomsen's correction. The latter, for instance, obtains the number 57610 c. for H = 1·0025, from which the number 57470 c. is obtained for H = 1. Compare also *Thermochem. Unters.* ii. 55.

cases we cannot even approximately estimate how much of the observed calorific effect is due to disgregation, and it is impossible to say whether it is greater or less than that due to affinity.

§ 222. Our ignorance respecting the phenomena of disgregation renders the exact investigation of the calorific effects accompanying the action of affinity an exceedingly difficult one. As a rule it is not known whether the production of heat observed in a chemical change has been produced by the saturation of chemical affinity, or whether it owes its origin in part to other potential or kinetic energy, and it still remains very doubtful whether the kinetic energy produced by the saturation of affinity has appeared as heat, or whether greater or smaller quantities have been employed in the increase of the disgregation.

It is, in fact, doubtful whether heat produced by affinity can be separated from that produced by disgregation even in the abstract, let alone experimentally. It is quite possible that both arise out of operations quite analogous in character, the extremes of which exhibit marked differences; but the contrasts in these cases are so gradually adjusted by intermediate members that no sharp boundary can be drawn between them. This conception finds considerable support in the observation that those chemical changes accompanied by positive calorific effect are, as a rule, attended by contraction, a diminution of the space occupied by the active bodies, and in such cases where a negative calorific effect is produced, an expansion is usually observed. These changes of volume accompanying chemical change have latterly been investigated by W. Müller Erzbach,[1] who arrives at the conclusion that, almost without exception, contraction takes place in all cases where an element or radical to which, from its chemical behaviour, we attribute a stronger affinity, expels another, to which we are accustomed to ascribe a weaker affinity.

To cite a few examples from the numerous cases collected

[1] V. Müller-Erzbach, *Pogg. Ann.* 1870, cxxxix. 287; 1873, cxlix. 33; 1875, cliv. 196. *Programm Nr.* 606 *der Hauptschule zu Bremen*, 1879; *Ber. d. deut. chem. Ges.* 1880, 1658; 1881, 217; 1882, 1301; 1883, 758; *Wied. Ann.* 1881, 522; *Liebig's Ann.* 1881, ccx. 196; 1883, ccxxi. 125.

together by Müller Erzbach: when a metal A can expel another, B, from its compounds with C, then in almost every case the relations between the volumes measured in the solid state are—

$$V(BC) + V(A) > V(AC) + V(B).$$

When iodine is expelled by bromine, and this latter by chlorine from their compounds with another element E, then the volumes are—

$$V(EI) + V(Br) > V(EBr) + V(I)$$
$$V(EBr) + V(Cl) > V(ECl) + V(Br).$$

On the other hand, many of the oxygen compounds of the halogens exhibit a contraction of the total volumes, when in accordance with the strength of the affinities chlorine is expelled by bromine and this by iodine. Müller Erzbach considers that we have here a suitable method of measuring the strength of affinities, since the changes taking place in this sense are always accompanied by contraction. It is not, however, according to his views an absolute measure, but still it is better than that of the calorific effects accompanying such changes. Those who will not go so far as to prefer to measure affinity by the contraction rather than the calorific effect, must acknowledge that both of these phenomena stand in a very near relationship to the primal cause of chemical change.

But different explanations may be given as to the existence of this causal connection; the one most generally accepted is that the stronger affinity communicates a greater velocity to the atoms, which brings them nearer to one another, and by the series of collisions a greater amount of heat is produced. It is also permissible to suppose that the atoms produce heat by coming in contact with one another, because their approximation renders a part of their individual motion impossible, consequently this motion is converted into heat. The important difference between these views, otherwise not very dissimilar from one another, is to be found in the fact that, according to the former, the contraction as well as the calorific effect is dependent upon the reciprocal action of the combining substances, whilst according to the latter the part

taken by each separate body in both operations is, or may be, independent of the other.

§ 223. Different observations, amongst which we may mention the results obtained by J. Thomsen[1] in the determination of the heat of neutralisation of acids and bases in dilute solutions, show that the thermal effect produced by one body is independent of the nature of the substance on which it acts. Under the assumption that the acid, base, and salt are soluble and remain dissolved, or that the heat absorbed by the dissolution of one of these substances, or that produced by the production of a precipitate, has been deducted, then it follows that the heat of neutralisation is dependent upon the nature of the base, as well as upon that of the acid; still there are many acids which produce the same calorific effect with the same base, and also different bases may produce the same calorific effect with the same acids. The difference of the heat of neutralisation of two acids is, with two exceptions, very nearly or exactly the same, no matter what base may have been neutralised by them, and also the difference of heat of neutralisation of two bases is independent of the nature of the acid used to neutralise them.

Thus, for instance, in neutralising an acid by caustic soda, for every 2NaOH, 630 units of heat are produced more than that produced by the equivalent quantity of baryta. Sulphuric acid gives for H_2SO_4, 3530 to 3580 thermal units more than the equivalent quantities of hydrochloric acid, 2HCl, of nitric acid, $2HNO_3$, of thio-sulphuric acid, $H_2S_2O_6$, or ethyl hydrogen sulphate, $2EtHSO_4$, and about 16,000 heat units more than the equivalent quantity of the mono-basic sulphuretted hydrogen, 2HSH.

From these observations it follows that the heat of neutralisation acccompanying the formation of a salt from an acid and base represents the sum of two calorific effects, one of which is determined by the nature of the acid, the other being dependent upon the nature of the base. The phenomenon of neutralisation appears, therefore, to be the sum of two quite distinct changes of state of each of the two reacting

[1] *Pogg. Ann.* 1871, cxliii. 354, &c.: *Thermochemische Untersuchungen*, 1882, i. 422.

HEAT OF FORMATION OF SALTS (PRODUCED IN AQUEOUS SOLUTIONS FROM THEIR ELEMENTS).

Metals	Chlorides ($\overset{''}{R}$, Cl_2, Aq)	Bromides ($\overset{''}{R}$, Br_2, Aq)	Iodides ($\overset{''}{R}$, J_2, Aq)	Hydrates ($\overset{''}{R}$, O_2, H_2, Aq)	Sulphhydrates ($\overset{''}{R}$, S_2, H_2, Aq)	Sulphates ($\overset{''}{R}$, S, O_4, Aq)	Dithionates ($\overset{''}{R}$, S_2, O_6, Aq)	Nitrates ($\overset{''}{R}$, N_2, O_6, Aq)
Li_2 .	204500	182620	152200	234880	132240	340220	404670	223830
Na_2 .	193020	171160	140600	223620	120980	329050	393440	212440
K_2 .	202340	180460	150040	232920	130280	338260	402710	221920
Mg .	186930	165050	134630	—	114880	322590	387610	203300
Ca .	187230	165360	134940	217620	115250	322810	387990	206580
Sr .	195690	173810	143460	226140	123770	—	396520	215200
Ba .	196810	174940	144520	227120	124750	332490	397600	216840
Cu .	62710	40830	—	—	—	198370	263540	82230
Ag_2 .	—	—	—	—	—	162800	227890	46600
Zn .	112840	90960	60540	—	—	248500	313770	132330
Cd .	96250	75640	47870	—	—	232290	—	116120
Hg .	59860	—	—	—	—	—	—	—
Tl_2 .	76960	—	—	107520	—	212700	—	96360
Sn .	81140	—	—	—	—	—	—	—
Pb .	75970	54410	—	—	—	—	276770	97890
Mn .	128000	106120	75700	—	—	263660	328830	147540
Fe .	99950	78070	47650	—	—	235610	—	—
Co .	94820	72940	42520	—	—	230480	—	114360
Ni .	93700	71820	41400	—	—	229360	—	113240

substances, and not as a consequence of the reciprocal action of both, that is their attraction or affinity. It is therefore very improbable that the heat of neutralisation arises from the potential energy of chemical affinity. It appears rather to be produced by quite distinct changes of energy, independent of those of affinity, and indeed possibly from the kinetic energy of the reacting substances.

All acids and bases do not exhibit this constant difference of heat of neutralisation; more especially is this the case with some of the weaker—for instance, acetic acid. Still, these differences cannot be considered as produced by other causes than those operating in the other cases.

§ 224. Inasmuch as the heat of formation of a salt is compounded of that of the acid together with that of the base, and that of the heat of neutralisation, then this discovery of Thomsen's shows that the total calorific effect attending the formation of a salt in aqueous solutions from its elementary constituents represents the sum of two constant quantities, one of which alone is dependent upon the nature of the metal, the other upon that of the negative constituent.

The preceding table contains these calorific effects for nineteen metals, in the formation of different salts, calculated from Thomsen's determinations. The numbers in each case correspond to two equivalents of metal. Their meaning will be intelligible from the headings attached to each column.

Of all the metals investigated, lithium produces the greatest amount of heat when it passes from the metallic state into a salt dissolved in water; the calorific effect exceeds that of the other metals by quantities represented in the table on the following page.

The 'calorific effect,' in the case of lithium, exceeds that of any other metal by almost the same amount, irrespective of the nature of the element with which it unites. The same applies to the negative elements. For instance, gaseous chlorine, when it forms a chloride soluble in water, produces, for every two atoms, by its combination with two equivalents of a metal and solution of the chloride in water, 9300 ^{c} less than 2 atoms of N, and 6 atoms of O, forming a nitrate of the same metal, and about 200200 ^{c} less than 2 atoms of S, and 6

(*a*). Differences of Calorific Effects from those of Lithium Salts.

Metal	Chloride	Bromide	Iodide	Hydroxide	Sulph-hydrate	Sulphate	Dithionate	Nitrate
Li_2	0	0	0	0	0	0	0	0
Na_2	11480	11460	11600	11260	11260	11170	11230	11390
K_2	2160	2160	2180	1960	1960	1960	1960	1910
Mg	17570	17560	17570	—	17630	17630	17060	17530
Ca	17270	17260	17260	17260	16990	17410	16680	17250
Sr	8810	8810	8740	8740	8470	—	8150	8630
Ba	7690	7680	7680	7760	7490	7730	7070	6690
Cu	141790	141790	—	—	—	141850	141130	141600
Ag_2	—	—	—	—	—	177420	176780	177230
Zn	91660	91660	91660	—	—	91720	90900	91500
Cd	108250	106980	104330	—	—	107930	—	107710
Hg	144640	—	—	—	—	—	—	—
Tl_2	127540	—	—	127360	—	127520	—	—
Sn	123360	—	—	—	—	—	—	—
Pb	128530	128210	—	—	—	—	127900	125940
Mn	76500	76500	76500	—	—	76560	75840	76290
Fe	104550	104550	104550	—	—	104610	—	—
Co	109680	109680	109680	—	—	109740	—	109470
Ni	110800	110800	110800	—	—	110860	—	101590

atoms of O, forming the dithionate of the same metal; the other elements behave in a similar manner; hence we may form a table similar to the above, which would contain the differences by which the calorific effects of all the salts of each metal exceed that of one of them—for instance, that of the chlorides. This has been done in the following table:—

(*b*). Difference in the Calorific Effects from those attending the Formation of Chlorides.

Metal	Chloride	Bromide	Iodide	Hydroxide	Sulph-hydrate	Sulphate	Dithionate	Nitrate
Li_2	0	−21880	−52300	+30380	−72260	+135720	+200170	+19330
Na_2	0	21860	52420	30600	72040	136030	200420	19420
K_2	0	21880	52300	30580	72060	135920	200370	19580
Mg	0	21880	52300	—	72050	135660	200680	19370
Ca	0	21870	52290	30390	71980	135580	200760	19350
Sr	0	21870	52230	30450	71920	—	200930	19510
Ba	0	21870	52290	30310	72060	135680	200790	20030
Cu	0	21880	—	—	—	135660	200830	19520
Zn	0	21880	52300	—	—	135660	200930	19490
Cd	0	21610	48380	—	—	136040	—	19870
Tl_2	0	—	—	30560	—	135740	—	19400
Pb	0	21560	—	—	—	—	200800	21920
Mn	0	21880	52300	—	—	135660	200830	19540
Fe	0	21880	52300	—	—	135660	—	—
Co	0	21880	52300	—	—	135660	—	19540
Ni	0	21880	52300	—	—	135660	—	19540

The differences indicated in the same lines or columns in the last two tables are very nearly equal. The small differences exhibited by them are generally, but not in every instance, within the limits of experimental errors. In the case of cadmium, the differences of the heat of neutralisation with different acids,[1] and accordingly the total heat of formation of the salts, vary; the exception exhibited by lead nitrate is the immediate result of the observation that lead oxide produces more heat with nitric acid than with hydrochloric [2] acid, whilst, otherwise, both acids have equal heats of neutralisation; lead dithionate, by another method of calculation, also forms an exception. The heat of neutralisation of this acid with soda was found equal to that of hydrochloric acid and of nitric acid.[3] If the heat of neutralisation of lead oxide be taken as equivalent to that of the former, then the number contained in the table is obtained; if, as has been done by Thomsen,[4] it is taken as equal to nitric acid, then the heat of formation of the dithionate will be 279110 °, a number forming an exception to the series.

Premising, as we may, that these observed regularities will hold in the case of salts of metals and acids not investigated, the calorific effects accompanying the formation of these salts in aqueous solutions may be calculated with fair approximation by adding the differences in the tables a and b to those of lithium chloride, just as the composition of neutral salts may be determined from a knowledge of the equivalents of acids and bases.

If we denote by α (R) the calorific effect due to a metal, and by β (Q) that due to the constituents of an acid, then the calorific effect produced in the formation and solution of the salt (R, Q) will be represented as follows:—

$$(R, Q, Aq) = (Li_2, Cl_2, Aq) - \alpha (R) + \beta (Q).$$

When, for instance, the dithionates of nickel or cobalt are formed from one atom, Ni or Co, two atoms, S, and six atoms,

[1] J. Thomsen, *Thermochemie*, iii. 279, 545.
[2] *Ibid.* i. 378, 386, 444; iii. 328.
[3] *Ibid.* i. 174.
[4] *Ibid.* iii. 519.

O, and dissolved in water, the calorific effects accompanying their formation will be as follows:

$$(Co, S_2, O_6, Aq) = 204500^c - 109680^c + 200800^c = 295620^c$$

$$(Ni, S_2, O_6, Aq) = 204500^c - 110800^c + 200800^c = 294500^c$$

numbers, which are fairly accurate.

The conditions are not so simple in the case of the formation of salts in the solid state, and even in solution the heats of formation of many salts, especially of those of weaker acids and bases, do not exhibit a similar regularity, which is, perhaps, to be explained by a difference in the constitution of their solutions.

§ 225. The experiments of W. Ostwald[1] afford a similar insight into the knowledge of the operation of neutralisation. Ostwald's method of experiment consists in dissolving acid and base in so much water that the solution of each equivalent weight in grams weighs a kilogram; the solutions are mixed, and the changes in volume accompanying their action upon one another determined; when expansion takes place this is regarded as positive, and a contraction as negative. These observations show that the changes in volume associated with neutralisation vary with the nature of the acid, as well as with that of the base; if, however, the different bases are employed to neutralise one and the same acid, then, for two different bases, the expansion exhibits the same difference, whatever be the nature of the acid neutralised, and also the difference of the expansions associated with the neutralisation of two acids is independent of the base neutralised. In the following table, under the headings potash, soda, ammonia, are given the expansions which accompany the neutralisation by these bases of the acids mentioned in the first column, and at the same time the differences of these expansions, which are very nearly equal for all acids.

[1] *Volumchemische Studien*, Magister Dissertation, Dorpat, 1877; Doctor Dissertation, 1878; *Pogg. Ann.* 1876, Erg.-Bd. viii. 154; *Journ. f. prakt. Chemie*, a series of papers from 1877.

	Potash	K—Na	Soda	Na—Am	Ammonia	K—Am
Nitric acid	+20·05	0·28	+19·77	26·21	− 6·44	26·49
Hydriodic acid	+19·80	0·26	+19·54	25·28	− 6·44	26·24
Hydrobromic acid	+19·63	0·29	+19·34	25·90	− 6·56	26·19
Hydrochloric acid	+19·52	0·28	+19·24	25·81	− 6·57	26·09
Trichloracetic acid	+17·36	0·29	+17·07	25·73	− 8·66	26·02
Dichloracetic acid	+12·95	0·25	+12·70	25·67	−12·97	25·92
Formic acid	+12·36	0·21	+12·15	25·74	−13·59	25·95
Monochloracetic acid	+10·85	0·23	+10·63	25·72	−15·09	25·94
Glycolic acid	+ 9·62	0·10	+ 9·52	26·01	−16·49	26·11
Acetic acid	+ 9·52	0·23	+ 9·29	25·55	−16·26	25·78
Lactic acid	+ 8·27	0·14	+ 8·13	25·87	−17·74	26·01
Propionic acid	+ 7·83	0·15	+ 7·68	25·50	−17·82	25·65
Butyric acid	+ 6·98	0·14	+ 6·84	25·47	−18·63	25·61
Isobutyric acid	+ 6·30	0·13	+ 6·17	25·44	−19·27	25·57
	Mean	0·21		25·75		25·97

The following table expresses by how much the expansion accompanying the neutralisations by the several acids exceeds that of isobutyric acid, which is the smallest of all. It is evident that these differences are also almost independent of the nature of the base.

	Potash	Soda	Ammonia	Mean
Nitric acid	13·74	13·60	12·83	13·39
Hydrochloric acid	13·22	13·07	12·70	13·00
Trichloracetic acid	11·06	10·89	10·60	10·85
Dichloracetic acid	6·65	6·53	6·30	6·49
Monochloracetic acid	4·55	4·45	4·18	4·39
Acetic acid	3·22	3·11	3·01	3·11
Lactic acid	1·97	1·96	1·53	1·82
Propionic acid	1·53	1·50	1·45	1·49
Butyric acid	0·68	0·67	0·64	0·66

If we take the smallest expansion observed in neutralisation, that of isobutyric acid, and represent it by a, and that produced by ammonia by b, then

$$a + b = 19{\cdot}27\ ;\ b = -(a + 19{\cdot}27)\ ;$$

from the mean of the differences given above, the expansion accompanying neutralisation for potash and soda is as follows:—

Potash, $b + 25{\cdot}97 = 25{\cdot}97 - 19{\cdot}27 - a = 6{\cdot}70 - a$
Soda, $b + 25{\cdot}75 = 25{\cdot}75 - 19{\cdot}27 - a = 6{\cdot}48 - a$,

and for the acids the following values are obtained :—

Nitric acid . . .	$a + 13{\cdot}39$	Acetic acid . . .	$a + 3{\cdot}01$
Hydrochloric acid .	$a + 13{\cdot}00$	Lactic acid . . .	$a + 1{\cdot}82$
Trichloracetic acid .	$a + 10{\cdot}85$	Propionic acid . .	$a + 1{\cdot}49$
Dichloracetic acid .	$a + 6{\cdot}49$	Butyric acid . . .	$a + 0{\cdot}66$
Monochloracetic acid .	$a + 4{\cdot}39$	Isobutyric acid . .	a —

Since the constant a occurs in all these expressions, we cannot determine it, nor are we in a position to say whether it is positive or negative, or whether it represents a contraction or expansion ; still, without this knowledge, we obtain no unimportant clue to the operation of neutralisation. The most remarkable result contained in these numbers under consideration is, that in the formation of a salt, each acid and each base exercises in all cases quite a distinct influence upon the volume of the solution, so that the change in volume is composed of expansions or contractions, characteristic of both the acid and the base.

Since Ostwald has observed that the changes of refractive power brought about by neutralisation are quite similar to those phenomena attending the changes of volume, he concludes that the formation of a salt from an acid and a base belongs to that class of chemical operations in which the change of physical state produced by the act of combination has a constant value for every constituent entering into the combination, and is independent of the other constituents with which the first combines.

Ostwald, at the same time, draws attention to the fact that the heat of neutralisation, calculated for the equivalent weight, is usually so much the greater the smaller the expansion or the greater the contraction accompanying the neutralisation. Thus, for some organic acids, the following values have been obtained :—

	Expansion on neutralising with		Heat of neutralisation[1]
	KOH	NH_3	
Formic acid . .	+12·36	−13·60	13380
Acetic acid . .	+ 9·52	−16·26	13330
Propionic acid .	+ 7·83	−17·82	13340
Butyric acid . .	+ 7·01	−18·63	13660
Valerianic acid .	—	—	13980

[1] Berthelot, *Ann. Chim. Phys.* [5] 1875, vi. 326.

A similar remark applies to many inorganic acids, for an equivalent of which we have the following values :—

Acid	Expansion on neutralising with		Heat of Neutralisation (Thomsen, 1869)
	KOH	NH_3	
HNO_3	+ 20·05	− 6·44	13620 cal.
HCl	+ 19·52	− 6·57	13740 ,,
$\frac{1}{2}H_2SO_4$	+ 11·90	− 14·35	15690 ,,
HF	—	—	16270 ,,

This rule is not so generally applicable that one may conclude the heat of neutralisation to be always greater, the smaller the expansion; the above examples, however, show that, as already mentioned, both phenomena are very nearly associated with one another.

These remarkable observations of Thomsen and Ostwald, relating to the neutralisation of acids and bases, and the formation of salts in dilute aqueous solutions, are, however, capable of a still more extended application. Since the phenomena associated with the formation of salts, the calorific effect, the change of volume, and of refractive power, &c., are made up of two parts, one of which is dependent alone on the nature of the positive constituent, the other on that alone of the negative, and these being further both independent of one another, it follows that they cannot be attributed to reciprocal action, and are, therefore, not due to affinity. For, supposing these phenomena to be influenced by the strength of the affinity, then, for instance, chlorine by its union with potassium, or copper, or other elements, could not always have a constant influence on the calorific effect. These facts should rather be regarded as indicating that every free element, every acid, and also every base, contains a fixed amount of energy, which in the act of combination is in such a condition that it may in part be utilised in the production of change of the disgregation or liberated as heat. This energy is not produced by the affinity, but rather set at liberty by it. Thus, chemical affinity effects the combination of substances in a manner similar to that in which a spark, in igniting a barrel of gunpowder, causes an explosion, but has no influence

on the violence of the outburst, which is dependent alone on the amount of the powder.

§ 226. To the adherents of the older views on this subject, this undoubtedly unexpected but undeniable deduction demonstrates the necessity for care in attempting to answer the question as to the nature of the causal connection between the calorific effects accompanying chemical changes and the affinity of the atoms for one another. This question is one which latterly has frequently been the subject of discussion, more especially from the standpoint that affinity is a power of attraction residing in the atoms, and that the thermal effects represent the conversion of the potential energy of this power into kinetic; in such views is to be found the main support of the doctrine that when the atoms act in the sense of the stronger affinities a positive calorific effect is produced, provided this is not influenced by any change associated with the chemical changes.

Inasmuch as from this point of view the stronger affinity regarded as attraction must necessarily produce the greater calorific effect, the idea has obtained considerable support that the atoms, when yielding only to the action of their own powers, always produce those compounds with the formation of which the greatest development of heat is associated. This, in fact, appears to take place in many cases, but that it does so in accordance with law, no one has, as yet, dared to maintain, although such a law might appear evident and desirable. Observation has shown, not unfrequently, the existence of chemical changes accompanied by an absorption of heat, without the possibility of, in all cases, explaining this away by the characters of the accompanying physical phenomena; those investigators who have taken up this question have, as a rule, expressed themselves very cautiously in this matter.

J. Thomsen expressed in 1853,[1] and in 1873[2] repeated the following views on this subject: 'Every simple or complex action of a purely chemical character is associated with a production of heat.'

Alexander Naumann[3] in 1869 expressed himself as follows:

[1] *Pogg. Ann.* 1854, xcii. 34. [2] *Ber. d. deut. chem. Ges.* 1873, vi. 425.
[3] *Lieb. Ann.* 1869, cli. 158.

that 'with few exceptions, capable of being otherwise explained, those chemical changes which must take place with an absorption of heat are, so to speak, indirect changes. That is to say, they occur simultaneously, and are dependent upon other changes which are themselves accompanied by a production of heat.'

In giving the following rule, Berthelot[1] goes considerably further. 'Every chemical change which is completed without the interposition of external energy will always tend to the production of that body, or that system of bodies, developing the maximum quantity of heat.'

This statement has been reproduced in some of the newer text-books in a much more assertive and dogmatic form. It has been thoroughly criticised by B. Rathke, and its validity and range considerably narrowed, more especially the law maintained by Berthelot and designated by him as the 'Principe du travail maximum.' From the facts mentioned in §§ 223 and 224 neither of these statements can claim to be regarded as axioms, requiring no proof; but even when based upon the earlier view, which in the author's opinion is no longer tenable, the application of either of these views depends considerably upon the interpretation of certain phrases contained in the statements. That of Thomsen is dependent upon what is understood by an 'action of a purely chemical character,' whilst the application of that of Berthelot depends upon the meaning given to the words 'tends towards,' &c. ('tend vers la production,' &c.). If the expression, 'actions of a purely chemical character,' be understood to describe such as take place without the aid of physical forces; then those decompositions produced by heat, in which the kinetic energy of heat acts in separating the combined atoms, cannot any longer be regarded as purely chemical actions. This, however, stands in direct contradiction to the usual mode of expression, according to which the formation of a compound, as well as its decompositions, are usually spoken of as chemical actions. Whilst the differences, so far as Thomsen's propositions are concerned, are merely dependent upon the meaning to be assigned to certain definitions, there are greater and more

[1] *Essai de Mécanique chimique, fondé sur la Thermochimie*, ii. 421, 1879.

material differences in respect to the doctrines of Berthelot. Although one may allow the existence of a certain tendency to form the compound which produces the greatest amount of heat, or that such a tendency may be conceived, still, it must be admitted that in innumerable cases this tendency is not only never realised, but that its existence cannot be detected.

Berthelot has thoroughly discussed a large number of hose cases which form exceptions to his doctrine, and has attempted to explain away the discrepancies, and thus establish the validity of his views. Although these efforts have been successful in many cases, still, in others facts have been strained and arbitrarily interpreted, not unfrequently resulting in a contradiction in terms. Whilst referring the reader for a complete discussion of this matter to Rathke's [1] criticism, still, an endeavour will be made in the following to show that, from a general point of view, there are, and must be, many cases of chemical change which are not, and cannot be accounted for by Berthelot's doctrine.

§ 227. This doctrine rests on two assumptions, first, that the atoms, when unhindered by external forces, behave as if possessed of the stronger affinities, and secondly, that such a movement always produces a positive caloric effect. The two parts of this doctrine do not necessarily harmonise. The first of these is the outcome of an obsolete view, in accordance with which the atoms are regarded as material particles at rest. Granting this assumption, and presupposing that the reciprocal attractions (affinities) decrease in accordance with some law, at any rate, very quickly, as the distances separating them, then two atoms, A and B, which for simplicity are supposed to be monovalent, so soon as they are brought sufficiently near for the attractions to come into play, will then move towards one another, and by impact their potential energy will be completely converted into kinetic, which may entirely or partially assume the form of heat. Now, suppose a third atom C, the affinity of which for A exceeds that of B, is brought into their vicinity, no change will take place so

[1] *Ueber die Principien der Thermochemie und ihre Anwendung*, Halle, 1881; *Abh. d. Naturf. Ges. zu Halle*, xv.; Wiedemann, *Beiblätter*, 1881, v. 183.

long as the distance of separation between A and C remains sufficiently great to render their mutual attraction less than that between A and B. But let C be brought sufficiently near, then it will combine with A, and, as we have supposed A to be monovalent, B is expelled from the compound. The kinetic energy thereby produced is equivalent to the potential energy existing between A and C, minus the amount of work required for the separation of A and B. Under these conditions a decomposition of the compound AC by B is entirely impossible. It would, therefore, follow that the stronger atom would invariably expel the weaker, so soon as it is brought sufficiently near to the combination, but it cannot be expelled by the weaker, and Berthelot's proposition could be unconditionally accepted.

The conception upon which this representation rests does not in any way correspond to the true character of the chemical elements and their compounds. Atoms and molecules are not material particles at rest, but particles in very rapid motion, and, indeed, every molecule has not only movements as a whole, but its individual parts, the atoms, are possessed of special motions, which are, however, limited to the extent that none of them can be separated beyond a fixed distance. So the form and intensity of the motions of the molecules, as well as of the atoms, depends not only upon their material nature, but, in the first place, on the temperature, and also, at least very frequently, if not invariably, upon the space occupied by a given quantity of the matter. As to the form of the molecular motions, fairly accurate assumptions may be made, especially in the gaseous or vaporous condition (see §§ 13–15); of other forms of molecular movement we know considerably less. Of the forms of the motions of the atoms in the molecules we are practically without information; *à priori* it may be maintained that the molecular, as well as the atomic movements, are either of such a nature that their kinetic energy remains invariably constant, or are of such a character that this alternately increases and decreases at the expense of the so-called tension or potential energy existent in them. The first case would be illustrated by an atom rotating about itself in circular paths, or by several rotating around one another

or some common centre ; in the latter case, on the other hand, the paths described by the atoms would not be circular, but elliptical, or several atoms would perform motions backward and forward in a manner somewhat similar to that of an iron ball suspended between the poles of a strong magnet, when set in motion in a line at right angles to the line joining the poles.

However these movements be conceived, such conceptions will have the greatest probability in which a portion of the kinetic energy passes at one time into potential, and this again into kinetic, in other words, movements by which the attracting atoms are at one time brought nearer, at another removed further from one another. That the movements are, as a rule, of this character, follows from the action of heat in effecting decompositions, already discussed.

If the movements of the atoms in the molecule are of the kind described, then the decomposibility of the molecules will vary according to the position of the atoms at any particular moment. It is, therefore, theoretically conceivable that one and the same molecule may in one case be decomposed by another whilst at other times it may not be so acted upon by the same substance, without our being able to detect a difference in the external conditions, more especially in that of temperature.

Taking again as the simplest example the phenomena resulting from the action of an isolated atom C upon a molecule AB consisting of monovalent atoms, which, for simplicity's sake, we may suppose to be in the gaseous state, consequently containing material particles moving in rectilineal paths with great velocity ; then different actions would result from the impact of AB on C. One of the possible results of this would be, that whilst A and B are removed from one another as far as possible, and consequently their kinetic energy in part converted into potential, C might strike A by reason of its great velocity, and so remove this atom from out of the sphere of B's action, and itself unite with A.

A portion of the kinetic energy of C would thereby be employed in overcoming the affinity of A to B, but at the same time heat or some other form of kinetic energy would result from the affinity of A to C.

Whether in the formation of the systems, by the action of the three atoms, the kinetic energy is greater or less than that of the system before their action, will depend upon whether C or B produces more heat by its combination with A: in order that the change may take place, it is evident that it is unnecessary that

$$(AC) > (AB),$$

for C may supply in kinetic energy what is wanting in affinity. The temperature will be lower after the change than before, but this does not make the change impossible.

§ 228. Passing now to the consideration of larger masses, then the case depicted above is only one amongst numerous other possible actions. For the final result of the interaction will be dependent upon the fact, whether the interchange takes place at all, if seldom or frequently, and more especially will it be determined by the circumstance, whether this change takes place more frequently than the opposite one, viz. the expulsion of C by B from its combination with A.

One might now try to conceive that when the affinity

$$(AB) > (AC),$$

then the change

$$AC + B = AB + C$$

would more easily and consequently more frequently take place than the reverse

$$AB + C = AC + B.$$

So that every quantity of the compound AC would, as soon as it is produced, be immediately decomposed, and finally the change corresponding to the stronger affinities must obtain the upper hand. This supposition is, however, theoretically entirely unnecessary, inasmuch as the possibility and the feasibility of such decompositions are not dependent alone on the strength of the affinities, but also upon other properties of the atoms and compounds, and likewise upon external conditions. A nearer consideration of the phenomena shows, that in order that the change may be brought about, it is not sufficient that the particles in their rapid movements to and fro should only meet, but that the nature of the impact is also of considerable importance. Supposing for instance that

C can unite with A in any position, but that B can only unite when A approaches it in some given position, then AC can form more quickly than AB. Any isolated atom A would therefore more quickly find an atom C, with which it can combine, whilst it might meet B a hundred times before the compound AB could be produced. Such a case would perhaps seldom occur with isolated atoms; but might more frequently occur in case of compounds consisting of several atoms, the compound radicals, for instance, which can only unite with an atom in a particular position. It would be useless to follow such considerations further; it may be considered sufficient to have shown that a chemical change is a complicated phenomenon, dependent upon a variety of conditions, and not determined alone by the so-called affinity.

In fact, many observations show, as the following sections will prove, that a chemical change very frequently is accompanied by one directly opposed to it, that, under exactly similar conditions combination and decomposition take place side by side, therefore, together with the change operating, in the sense of the stronger affinities, the opposite, which the weaker affinities tend to bring about, takes place, so that the condition striven for by the stronger affinities is never completely attained. One might indeed say that, when

$$(AB) > (AC),$$

then the change

$$AC + B = AB + C$$

is brought about by affinity, and the reverse

$$AB + C = AC + B,$$

taking place simultaneously, is due to the action of heat, therefore an external cause. This would, however, be nothing more than a play with words, for, without heat being produced very few, if any changes take place at all. But if heat aids both decompositions, then it is at the least arbitrary to say that the first is brought about by affinity aided by heat, and the second by heat aiding the weaker affinity of C to B.

If one should style as external energy the heat contained in the interacting substances, in the form of molecular motion, then most probably there is not any chemical change com-

pleted without the aid of external energy, at any rate, such could only be observed at absolute zero, viz. at—273° C.

§ 229. The second conception contained in Berthelot's doctrine, that the satisfying of the stronger affinities is invariably associated with a larger positive calorific effect, has perhaps never been doubted, but generally recognised as self-evident, although conclusive reasons for the necessity of such a supposition are not to be found. There are important theoretical reasons for laying down this principle, a principle which cannot, however, be derived with the same generality from observation.

Although the author has at all times advocated the value of hypotheses and theories and even the use of incorrect ones, and at the same time is willing to acknowledge that without the theoretical considerations upon which this doctrine is based we may not be in a position to dispose of the experimental data obtained by thermo-chemical investigations, still immediate danger may arise from too dogmatic an assertion of this doctrine, which is neither unassailable from a theoretic point of view nor experimentally proven, and thereby interfering with an unprejudiced view of the facts and hence staying the true advance of our knowledge.

The ideas upon which this and other doctrines of thermo-chemistry are based, have their origin in those which regarded the phenomena of molecular physics and of chemistry as entirely statical phenomena, as produced by particles possessed of forces of attraction resting in positions of equilibrium. Since that time the conceptions of physicists and chemists have entirely changed; kinetic theories have come to the fore and have revealed to us the properties of matter in a light hitherto undreamt of. The kinetic theory does not, as has already been pointed out (§ 227), allow of the doctrine of the equilibrium of atoms at rest; the conception of the action of affinities without that of the atomic motions, especially of heat, is a fiction which cannot be applied in any case coming under our observation. If these movements of the atoms are to be considered, then we must investigate what part in the observed calorific effects is to be attributed to them, and how much is due to the potential energy of the hypothetical force of affinity.

The facts described in §§ 224–226 make it appear extremely doubtful whether the atoms do really possess powers of attraction and consequently potential energy; it is more probable that the whole of the kinetic energy they give out is already their own as such. This being the case then the whole conception of affinity, upon which the doctrines of thermo-chemistry are based, requires to be completely reconstructed, and there can no longer be any talk of potential but only of kinetic energy.

Considering the doubtful position of these doctrines it appears requisite to regard them as problems wanting in proof, and to investigate without prejudice what chemical changes are accompanied by a positive and what by a negative calorific effect. Julius Thomsen has many years ago indicated this method as the right one, when he says:[1]

'In the different branches of Natural Science apparently very simple laws are frequently discovered; but an exact examination of these soon leads to the discovery of anomalies, the causes of which are to be found partly in faulty observations, partly in the imperfections of the law. So has it been with me in this case. The simple laws of thermo-chemistry agree with observations in so many instances that I have been thoroughly convinced of their near approximation to the truth. But a continued study of the phenomena brought to light numerous anomalies, and it was soon made evident from my own observations that the older investigations were in part too inexact to form substantial grounds for speculation. Instead of making useless speculations as to the cause of these anomalies, I chose, rather, the more difficult but by far more certain method, viz. by means of a comprehensive experimental investigation to collect new and reliable material.'

The science is not even to-day, ten years later, in a position to forsake this path. It is not her province to explain away the exceptions to the supposed laws, but to show impartially what are the cases in which the supposed law holds, where positive and where negative calorific effects are produced, and finally in what cases the amounts of heat produced correspond to the greatest possible amount which the re-acting bodies can produce. The more carefully this is performed, the sooner

[1] *Ber. d. deut. chem. Ges.* 1873, 428.

shall we arrive at the knowledge of those laws and rules which must supersede the present ones.

§ 230. An unbiassed examination of the observations shows that the supposition, that the stronger affinity corresponds to the greater heat production, is not by any means in every case confirmed.

It is, for example, not easy for any one to object to the supposition that those acids possess the greater affinity, which when in equivalent quantity with another in reacting simultaneously and under similar conditions upon an equivalent of a base, can combine with the larger portion of the base. The stronger acids, defined so in accordance with this idea, are by no means those which when neutralised by bases produce the larger amount of heat. On the contrary a large number of examples are known of acids which produce the greatest calorific effect when neutralised, yet these are expelled from their salts more or less completely by acids having a much smaller heat of neutralisation. The following table contains a series of mono- and di-basic acids arranged according to the values of their heat of neutralisation obtained by Thomsen,[1] and calculated as equivalent to two equivalents of sodic hydroxide (2 NaOH):

HEAT OF NEUTRALISATION OF ACIDS.

Hydrofluoric acid . . .	2 H . F	32540 c.
Sulphuric „ . . .	$H_2 . SO_4$	31380
Selenic „ . . .	$H_2 . SeO_4$	30390
Hypophosphorous „ . . .	$2 H . PH_2O_2$	30320
Dichloracetic „ . . .	$2 H . C_2HCl_2O_2$	29660
Sulphurous „ . . .	$H_2 . SO_3$	28970
Metaphosphoric „ . . .	$2 H . PO_3$	28760
Monochloracetic „ . . .	$2 H . C_2H_2ClO_2$	28540
Phosphorous „ . . .	$H_2 . PHO_3$	28450
Oxalic „ . . .	$H_2 . C_2O_4$	28280
Perchloric „ . . .	$2 H . ClO_4$	28160
Trichloracetic „ . . .	$2 H . C_2Cl_3O_2$	27840
Iodic „ . . .	$2 H . JO_3$	27620
Bromic „ . . .	$2 H . BrO_3$	27560
Chloric „ . . .	$2 H . ClO_3$	27520
Hydrobromic „ . . .	2 H . Br	27500
Hydrochloric „ . . .	2 H . Cl	27480
Hydriodic „ . . .	2 H . J	27360
Nitric „ . . .	$2 H . NO_3$	27360
Chloroplatinic „ . . .	$H_2 . PtCl_6$	27220

[1] *Thermochemische Untersuchungen*, i. 294, 422.

HEAT OF NEUTRALISATION OF ACIDS—*continued.*

Dithionic acid . . .	$H_2 . S_2O_6$	27070 c.
Selenious „ . . .	$H_2 . SeO_3$	27020
Propionic „ . . .	$2\,H . C_3H_5O_2$	26960
Ethyl sulphuric „ . . .	$2\,H . C_2H_5SO_4$	26920
Formic „ . . .	$2\,H . CHO_2$	26900
Acetic „ . . .	$2\,H . C_2H_3O_2$	26800
Hydrofluosilicic „ . . .	$H_2 . SiF_6$	26620
Periodic „ . . .	$H_2 . JH_3O_6$	26590
Malic „ . . .	$H_2 . C_4H_4O_5$	26170
Tartaric „ . . .	$H_2 . C_4H_4O_6$	25310
Chromic „ . . .	$H_2 . CrO_4$	24720
Succinic „ . . .	$H_2 . C_4H_4O_4$	24160
Carbonic „ . . .	$H_2 . CO_3$	20180
Boric „ . . .	$H_2 . B_2O_4$	20010
Arsenious „ . . .	$H_2 . As_2O_4$	13780
Hypochlorous „ . . .	$2\,H . ClO$	9980
Stannic „ . . .	$H_2 . SnO_3$	9570
Sulphuretted hydrogen . .	$2\,H . SH$	7740
Silicic acid	$H_2 . SiO_3$	5230
Hydrocyanic acid . . .	$2\,H . CN$	2770

Considering the usual behaviour of the above acids, no impartial observer would regard their arrangement in the above table as expressing correctly the strength of their affinities to bases. Although the substances grouped together at the end of the table undoubtedly belong to the weakest acids, still, those associated together at the commencement are by no means the strongest acids. The strongest acids at ordinary temperatures, viz. hydrochloric and nitric acids, are in fact to be found in the middle of the series following a number of the weaker acids, which, as will be more fully shown further on, can easily be expelled from their salts by these acids.

If the amount of calorific effect must be taken as a sign of stronger affinity, then we must necessarily conclude that the neutralising of acids by bases, the formation of salts in aqueous solutions, is in no way due to the action of chemical affinity. This strange conclusion can only be avoided by denying the dogma of the ratio between affinity and calorific effect, and by refusing to recognise the truth of the conception that there is a distinct difference between chemical changes accompanied by positive and those associated with negative calorific effects. This distinction would, in fact, frequently lead to separating substances nearly allied to one another, for numerous observations have shown that even with phenomena

distinctly analogous in character, in some cases heat is produced and in others cold. This has been shown by Thomsen in his measurements of the calorific effects produced by the decomposition of different salts by nitric or hydrochloric acids. Thus, while hydrochloric acid decomposes chromates, carbonates, fluosilicates, tartrates with a production of heat, under exactly similar conditions its decomposition of sulphates, sulphites, fluorides, and oxalates is associated with a considerable production of cold.

§ 231. Similarly, an entirely unbiassed criticism of many other numerous observations shows that although frequently, yet not invariably does it happen that the tendency to the formation of the combination of atoms producing the greatest amount of heat obtains, and that even when a change does take place, it does not of necessity follow that it is the one corresponding to that of the so-called maximum work. Substances can be brought into intimate contact with oxygen and kept with it for any length of time without any change taking place. Oxygen and hydrogen may be kept together any length of time, at ordinary temperatures, without forming water; free hydrogen and chlorine also, if kept entirely in the dark; iodine and sulphur may be separately distilled off from zinc unchanged, and even sodium retains its lustre in perfectly dry chlorine, despite the fact that by the union of these different substances, considerable amounts of heat are produced. Even when several substances are brought together under such conditions that combination may take place, frequently, but not invariably, is that compound produced, the formation of which is associated with the greatest heat formation. For instance, hydrogen and oxygen may be mixed with chlorine in any given proportion and the mixture exposed to the action of light, hydrochloric acid alone is formed, and not a trace of water, although the production of the latter would produce an amount of heat greater by half than that produced by the union of hydrogen and chlorine. This is not strange, because chlorine alone and not oxygen is able to combine with hydrogen under the influence of light. The electric spark can, however, cause hydrogen to combine with oxygen as well as chlorine. If an electric spark be passed through a mixture of

all three gases, the production of water is entirely dependent upon the quantity of chlorine. If the chlorine present is in sufficient quantity to combine with the whole of the hydrogen, then no trace of water is produced. Under similar conditions oxygen will unite with the whole of the hydrogen, in fact, a portion of the latter will combine with the oxygen, provided that the amount of chlorine present is not sufficient for the whole of the hydrogen in the mixture. Water is likewise produced when a jet of burning hydrogen is brought into a mixture of chlorine and oxygen; this arises from the fact that in the interior of the flame there is more hydrogen than the chlorine reaching it can unite with. Chlorine, as is well known, decomposes water in sunlight; oxygen, on the other hand, requires the aid of heat to decompose hydrochloric acid. In Deacon's process this latter decomposition, aided as it is by the action of copper sulphate, is never a complete one, despite the fact that it is associated with a development of heat.

Under these circumstances it is desirable that it should be determined by experimental investigation, under what conditions is the satisfying of stronger affinities accompanied by positive calorific effects, and when by negative calorific effects. Then only will it be possible to discover the laws which undoubtedly exist, and are still practically unknown, controlling the relation between affinity, volume, and calorific effect.

§ 232. Observations prove that changes associated with positive calorific effects occur more frequently than those accompanied by negative ones; still the relation of the two in various kinds of processes is a very different one. A large class of decompositions are known in which the negative calorific effects have been seldom or never observed, whilst in other instances such changes occur more frequently and in some cases they are as numerous as those cases associated with positive calorific effects.

As J. Thomsen[1] pointed out in 1854, although the data obtained at that time were still very incomplete, yet they sufficed to show that the power of a metal to decompose water in either the gaseous or liquid state depended chiefly upon the heat produced in its oxidation, and in such a manner

[1] *Pogg. Ann.* 1854, xcii. 36.

that only those metals decompose water which produce on oxidation an amount of heat greater than the heat of combustion of hydrogen, whilst those metals are unable to decompose water, the heat of oxidation of which is less than that of hydrogen.

The same law applies also to the expulsion of hydrogen by metals from other compounds, more especially acids,[1] which likewise takes place only when this decomposition gives rise to a positive calorific effect.

The precipitation of a metal from solutions of its salts by another metal usually takes place in such a manner that the metal which on solution produces the smaller positive calorific effect, is expelled from its compound by that metal which by its solution produces the larger positive calorific effect. Still exceptions to this rule have been observed.[2]

Substitution of other elements, replacement of one element by another, is, as a rule, associated with a positive calorific effect; an instance of which we have in the exchange of one halogen element for another. The combination of chlorine with metals and other electro-positive elements produces more heat than that produced by bromine, and this again than iodine; and in complete agreement with these facts, chlorine expels both of these elements from their compounds with electro-positive elements, and bromine iodine from its compounds. On the other hand, chlorine is expelled by iodine from its compounds with oxygen, a decomposition also attended by production of heat.

Similar statements can be made with respect to other elements, and hence the course of several groups of chemical changes can be predicted from the knowledge of the thermochemical behaviour of the elements and compounds in question, and, on the other hand, the course of a given decomposition indicates with some degree of certainty that the affinities thereby 'neutralised' produce a larger positive calorific effect than those opposing this change.

§ 233. This is by no means the general rule, for there are large groups of chemical changes known, some of which, although entirely analogous, result in a positive calorific effect,

[1] *Pogg. Ann.* 1854, xcii. 43, § 39. [2] F. Braun, *Wied. Ann.* 1882, xvii. 639.

whilst others give rise to negative effects. To these belong, for instance, the phenomena mentioned in § 230, viz. the expulsion of one acid from its compounds by another.

Not only can one and the same acid, for example, nitric or hydrochloric acid, expel certain acids from their salts with a positive calorific effect and others with a negative; but starting with two acids and a base we can prepare a combination which will produce heat, or a combination which would produce cold. Suppose the base be neutralised with sulphuric acid, the solution allowed to cool and when cold treated with hydrochloric acid, then by its action a negative calorific effect is produced; if the operations be reversed, then by the action of sulphuric acid upon the chloride a positive calorific effect is obtained. In the following sections it will be shown that the final result in the two cases is the same. One and the same state is, therefore, arrived at whilst in one case a positive calorific effect, in the other a negative result is obtained.

Sulphuric acid has a greater heat of neutralisation than hydrochloric acid, still the latter can expel the former from its salts, the completeness of the decomposition being dependent upon the relative amounts of the two acids and on external conditions. Gaseous hydrochloric acid or its concentrated solution decomposes sodium sulphate with such a production of cold[1] that this mixture is largely used as a freezing mixture. The production of cold depends in fact to a great extent upon the heat of neutralisation of hydrochloric acid being much smaller than that of sulphuric acid, and that the former becomes free, whilst the latter remains latent.

These and many other examples, as has been already mentioned in § 223, show that from a knowledge of the heat of neutralisation of the different acids, no reliable conclusions can be arrived at as to the ability of these acids to expel one another from their compounds, such as can be drawn in the case of the metals.

Decompositions accompanied by negative calorific effects are more frequent at high than at low temperatures. This fact is usually expressed by saying that the heat represents

[1] C. Hensgen, *Ber. d. deut. chem. Ges.* 1876, ix. 1671; 1877, x. 259.

the work necessary for the decomposition of the compound, or yields the kinetic energy required, which in the decomposition is converted into potential energy. A fundamental difference between decompositions requiring a red heat and associated with a negative calorific effect and those taking place at the ordinary temperature, does not exist; for in both cases the particles of the materials possess kinetic energy, a part of which with the lowering of the temperature is utilised in bringing about the decomposition. It is, therefore, at least inconsistent to regard decompositions of this kind taking place at high temperatures in a light different from quite analogous decompositions taking place at a lower temperature, and in fact to consider the former as abnormal and to try by various artifices to explain them away. The fact to be recognised is that chemical changes requiring for their completion the aid of heat can take place under various conditions, and that such changes do take place more frequently and the more easily the more heat there is to be disposed of, consequently at higher temperatures, but that such changes do not take place exclusively at high temperatures.

§ 234. Decompositions, associated with negative calorific effects, take place usually very easily in association with others producing heat, so that in the total effect more heat is produced than is used.

Whilst the expulsion of iodine from silver iodide by chlorine is entirely in accord with the greater amount of heat produced by chlorine in combining with the metals, still silver chloride is converted into silver iodide by hydriodic acid, thus—

$$AgCl + HI = AgI + HCl.$$

The heat of formation of silver chloride is greater than that of silver iodide, yet that of hydrochloric acid is greater than that of hydriodic acid, so that the total heat produced in the formation of silver iodide and hydrochloric acid is greater than that liberated in forming silver chloride and hydriodic acid, thus—

$$(Ag, I) + (H, Cl) > (Ag, Cl) + (H, I).$$

In this case the greater calorific effect corresponds to the

stronger affinity, when it is recognised that the affinity of iodine for silver, supported by that of chlorine for hydrogen, overcomes the stronger affinity of chlorine for silver, together with that of iodine for hydrogen—

$$\frac{\mathrm{AgCl}}{\mathrm{IH}} = \frac{\mathrm{Ag}}{\mathrm{I}} \Big| \frac{\mathrm{Cl}}{\mathrm{H}}.$$

Comparing this with the conversion of silver iodide into silver chloride by the following reactions,

$$\mathrm{AgI} + \mathrm{ClCl} = \mathrm{AgCl} + \mathrm{ClI}$$

or

$$2\mathrm{AgI} + \mathrm{ClCl} = 2\mathrm{AgCl} + \mathrm{II},$$

then it is easy to understand that between the two cases there is no contradiction, inasmuch as the affinity of chlorine for itself and for iodine must be much feebler than its affinity for hydrogen, and hence not only may we have the above inequality, but the following also :—

$$(\mathrm{Ag, Cl}) + (\mathrm{I, Cl}) > (\mathrm{Ag, I}) + (\mathrm{Cl, Cl}).$$

Adding both these together and removing the same terms from each side of the expressions, we obtain the following :—

$$(\mathrm{H, Cl}) + (\mathrm{I, Cl}) > (\mathrm{H, I}) + (\mathrm{Cl, Cl}),$$

of the truth of which no doubt can be entertained.

The formation of the different oxides and oxyacids of chlorine from chlorine and oxygen would result in a negative calorific effect. They cannot be so prepared, but may be obtained by reactions accompanied by the formation of metallic chlorides, which are produced with considerable evolution of heat, as when chlorine reacts on the hydroxides of alkali-metals :—

$$\mathrm{KOH} + \mathrm{ClCl} = \mathrm{ClOH} + \mathrm{KCl}$$
$$\mathrm{KOH} + \mathrm{ClOH} = \mathrm{ClOK} + \mathrm{HOH},$$

or we may have the following taking place simultaneously :—

$$\frac{\mathrm{Cl}}{\mathrm{Cl}} \Big| \frac{\mathrm{KOH}}{\mathrm{KOH}} = \frac{\mathrm{KCl}}{\mathrm{ClOK}} \Big| \frac{\mathrm{OH}}{\mathrm{H}}.$$

Decompositions of this character, in which a negative calorific effect is completely overcome by a greater positive one, and in

this way an interchange of the atoms which otherwise would be impossible is brought about, are indeed numerous, and are frequently utilised as means to prepare compounds which cannot, or can only with difficulty, be obtained in other ways. The text-books of chemistry abound with examples of this kind, so that those given above will suffice.

§ 235. Whilst in these decompositions one change determines the other in such a manner that neither is possible alone, but both must take place simultaneously, another series of phenomena have been brought to light, in which the changes taking place are not immediately dependent upon one another, and are not produced simultaneously, but take place successively, and their production is determined in such a manner that the first requiring an expenditure of work does not take place unless the conditions are such as to allow of the second, which produces heat or work, taking place. Such a case we have in that investigated by Naumann,[1] viz., the action of iodine upon hydrogen sulphide. When these substances react upon one another in presence of a large quantity of water then the following change takes place:—

$$H_2S + I_2 = 2HI + S,$$

which under these conditions is accompanied by a considerable evolution of heat. According to J. Thomsen[2] it is expressed thus:—

$$(H_2S : I_2 : Aq) = 28830^{cal},$$

in which Aq signifies the presence of a considerable amount of water. The calorific effect is composed of that accompanying the decomposition of hydrogen sulphide by iodine, and of that resulting from the solution of hydriodic acid in water. It may be expressed thus:—

$$(H_2S : I_2 : Aq) = (H_2S : I_2) + (2HI \,.\, Aq) = 28830^{cal}.$$

The heat of solution of hydriodic acid has been found to be—

$$(2HI, Aq) = 2 \times 19207 = 38414^{c},$$

[1] *Liebig's Ann.* 1869, cli. 145.

[2] Thomsen used a solution of iodine in dilute hydriodic acid, which does not influence the result, inasmuch as this dissolution takes place without producing heat. Naumann formerly used the less reliable results of Favre and Silbermann.

hence it follows—

$$(H_2S : I_2) = (H_2S : I_2Aq) - (2HI, Aq)$$
$$= 28830^c - 38414^c = -16534^c,$$

that is to say, the decomposition of hydrogen sulphide by iodine can only, in the absence of water, be effected by the application of heat.

Naumann's attempts to effect this decomposition without water were fruitless. He has found that a solution of iodine in carbon bisulphide is not acted upon by hydrogen sulphide, nor is hydriodic acid formed when dry hydrogen sulphide is brought into contact with iodine in the solid or gaseous state. Naumann[1] concludes that the explanation of the fact that iodine and hydrogen sulphide react upon one another only in presence of water, is to be found in the fact that the presence of water is associated with a further change accompanied by a liberation of heat, so that the total calorific effect, which is made up of in part negative and in part positive effects, is a positive one, and the final result is a liberation of heat. In support of this view, Naumann cites the fact, known for some time, and confirmed by his own observation, that a very concentrated solution of hydriodic acid is decomposed by sulphur with a production of hydrogen sulphide. Naumann has also observed that this reversal of the reaction commences at that point when the concentration of the hydriodic acid is such that its heat of solution, which decreases as the mass of hydriodic acid absorbed decreases, is approximately sufficient to neutralise the negative calorific effect attending the decomposition of hydrogen sulphide by iodine.

But to this, at the first sight, clear explanation is opposed a very considerable difficulty, inasmuch as it goes back to the obsolete idea of predisposing affinity. Hydriodic acid is formed, because when once produced it may find opportunity to equalise the expenditure of work on heat which has been required for its production; just as formerly it was thought necessary to suppose that zinc expelled hydrogen from acidified water, because its oxide so produced had in view its union with the acid to form a salt. The acceptance of such actions

[1] *Liebig's Annalen*, cli. 151.

on the part of non-existing substances does not now appear requisite, and consequently this explanation of the formation of hydriodic acid will require to be reconsidered. It is possible that the influence of water in commencing the decomposition of sulphuretted hydrogen by iodine is to be found in the absorption of this gas by water, which, accompanied as it is by a not inconsiderable development of heat, may produce such changes in its disgregation as to make it more able to take part in chemical changes, just as aqueous hydrochloric acid can effect changes which the liquid anhydrous acid cannot produce. An unstable compound with water might produce changes of this character.

But the phenomenon may be easily explained without resort to this hypothesis. The reaction has been shown to be reversible; in presence of excess of water and but little hydriodic acid the following takes place :—

$$SH_2 + I_2 = 2HI + S;$$

but when there is little or no water present the action is as follows :—

$$2HI + S = H_2S + I_2.$$

In the absence of water hydriodic acid and sulphur cannot exist side by side; a particle once formed is immediately decomposed again. If water is present then it will unite with the hydriodic acid, forming a compound or solution which can resist the action of sulphur. The action will not be reversed until the amount of hydriodic acid formed is greater than that with which the water can combine. This explanation of the decomposition may perhaps differ but slightly from the other; but it has the advantage that it rests upon the single phases forming the decomposition, and that it does not necessitate our assigning as cause for a given phenomenon the result of a subsequent action.

§ 236. This case which Naumann has investigated is one of special import, but by no means the only one of its kind. There are many chemical decompositions which may be entirely reversed, showing that Berthelot's doctrine is not one of general application, for if the given change

$$AB + CD = AC + BD$$

be associated with a positive calorific effect, then the reverse

$$AC + BD = AB + CD$$

must, when dissociated from all accompanying changes, be one which will produce a negative calorific effect. This is, in fact, borne out by numerous observations, some of which will be discussed in the subsequent sections of this work. It is clear that reactions of the second form will require heat or kinetic energy; but it cannot be maintained that this is invariably the cause of the reversal. Very frequently both changes take place side by side under similar external conditions, such as temperature, &c.; and in other cases a positive or negative calorific effect can be obtained at will by varying the proportions of the reacting substances.

Whilst the doctrine of 'maximum work' cannot lay claim to be of service in case of those reactions which are reversible, still it is possible it may find application in the case of those reactions which cannot be reversed. Hence it is highly important that all chemical changes should be so studied as to determine whether or no they can be reversed, and whether any real and substantial difference is to be found between such as are reversible and those which cannot be reversed. That reactions of both kinds do so occur cannot be denied, but a complete separation of the two is impossible in the present state of our knowledge, and may perhaps never be completely maintained, inasmuch as instances will be discovered of reactions standing midway between the two extreme cases.

The causes of the reversal are in part such as produce chemical changes in general, the causes mentioned in § 194, more especially heat, light, and electricity, to which must be added as a very important factor that to which Berthollet was the first to draw attention, viz., 'the influence of mass,' which will form the subject of the next part of this work. This powerful influence in chemical changes has for many years been overlooked, and its importance unappreciated, but latterly recent investigations have again brought it to the fore. A thorough investigation of the influence of mass will be of the greatest importance in leading to a knowledge of

chemical phenomena, inasmuch as it will yield the foundation of a kinetic theory of affinity, which may replace, or at any rate limit, the older statical theory.

It is at present an open question, to which no definite reply can be made, as to whether the present representation of affinity, as a force of attraction acting on material particles at extremely small distances, the conversion of the potential energy of which into kinetic energy produces heat of combination, would find a place in a fully developed kinetic theory. In the author's opinion it will in all probability be found impossible to embrace this view of affinity in such a kinetic theory.

This same question is most closely connected with the broader issue which has frequently been disputed, as to whether in nature such attraction and action at a distance exists at all, or whether all phenomena apparently resulting from such action may not have been produced by pressure and impact, and therefore be dependent on forms of kinetic and not potential energy. It is not necessary for the further advance of chemistry that this question should be decided at the present, for the laws ruling the cause of chemical phenomena, which we at present style affinity, may be investigated without a thorough knowledge of its nature. But in order that the disturbing influences of preconceived ideas may be avoided, it is indispensable that it should be steadily borne in mind that the generally accepted representation of the changes of potential into kinetic energy, and *vice versâ*, are in all probability pure fictions, and that in all likelihood the changes so represented are changes of one form of kinetic energy into another. Should the explanation of chemical calorific effects undergo change in the future, then not only will reliable determinations of the same be of value to the new theory, but will receive a far higher position than can be assigned to them in accordance with the views which obtain in the theory of chemistry at the present time.

XIII.

INFLUENCE OF MASS ON CHEMICAL ACTION.

§ 237. Just as chemical changes are influenced by heat, in other words by the intensity of the motion of the atoms and molecules taking part in them, so also are they affected by their number, that is to say, by the mass. In many cases a diminution of the mass of the substances taking part in a chemical change has an effect similar to that produced by a rise in temperature; and again, an increase of the mass will often suffice to equalise the effect produced by a rise in temperature, and to stay its action.

This co-relation between mass and heat is seen most clearly in the simplest effect of heat, viz. dissociation, in which the accumulation of products of dissociation hinders the dissociation just as a lowering of temperature would. This fact may be explained by supposing the state of incomplete dissociation to consist of a continual decomposition and simultaneous reproduction of the compound capable of being dissociated, and this latter phenomenon will happen the more frequently when the amount of the material present, necessary for its formation, is great. The observations hitherto made as to the influence of mass upon the dissociation of the greatest variety of substances, solid, liquid and gaseous, are quite in accord with this view.

When the molecules of a gas or vapour dissociate into smaller molecules, as is the case with nitric peroxide, then the re-union of the smaller molecules will take place the more frequently these particles meet one another, in other words the more dense the gas or the narrower the limits of space occupied by a given quantity of the gas. Since the density increases with the pressure, it follows therefore that the dissociation must diminish as the pressure due to the products

of this decomposition increases. The observations of Deville and Troost, as also those of Alex. Naumann,[1] show that in the case of nitric peroxide the same degree of dissociation can be attained by reduction of pressure as that produced by rise of temperature, as will be seen from the following table.

Temperature t	Pressure[2] p	Degree of decomposition	Difference		$\frac{\Delta p}{\Delta t}$
			of temperature Δt	of pressure Δp	
26°·7	0^{m}·756	20·0	10·7	0·527	49
16·0	0·229	20·0			
35·4	0·756	25·7	18·6	0·584	31
16·8	0·172	26·2			
39·8	0·756	29·2	19·0	0·602	31
20·8	0·154	29·3			
18·5	0·136	29·8			
49·6	0·756	40·0	27·1	0·655	24
22·5	0·101	39·0			

These numbers also demonstrate that the influence of pressure increases as the temperature rises.

§ 238. Numerous cases have been observed in which the dissociation of solid and liquid substances has been found to be influenced by the pressure due to the gaseous products of the dissociation. For each temperature there is a maximum of pressure, which, when the substance undergoing dissociation or one of the products is a solid, is frequently only reached very gradually, because the decomposition and also the re-combination require time, whilst the simple vaporisation and condensation of non-decomposible substances usually take place immediately. On the other hand, in the case of liquids losing gaseous constituents, the maximum of tension is very rapidly attained, and in such cases also the re-combination takes place almost as rapidly as is the case with non-dissociated vapours. Despite this characteristic of the solid state, which interferes in no small degree with an exact study of the phenomena, there can still be no reasonable doubt as to their general character.

In the case of solids, such dissociations taking place until a constant pressure due to the products of decomposition has

[1] Naumann, *Thermochemie*, 1882, p. 130.

[2] The absolute values of the pressure are not exact, but the differences are reliable.

been reached, have been observed; for example, in the case of the ammonium salts, notably the slow re-production in the case of the carbamate, in the case of the compounds of many salts and other substances with water, and with ammonia, also in the case of acid and normal carbonates, in the higher chlorides of many elements, in the oxides of the noble metals and other solids. In the dissociation of liquids, aqueous solutions have been studied, more especially those in which the pressures of aqueous vapour are less than those of pure water, as is the case when the body dissolved is capable of forming a compound with the solvent which can be dissociated.

When a compound capable of being dissociated is brought into an atmosphere of an indifferent gas, dissociation proceeds, more slowly than in vacuo, but attains the same, or very nearly the same point, so that the pressure due to the dissociation is added to the pressure of the indifferent gas. If, on the other hand, the substance is brought into an atmosphere of one of the products formed by its dissociation, then the pressure is raised by only a fraction of that of its dissociation in vacuum. This is probably explained by the fact that a portion of the gas constituting the atmosphere combines with one of the products of dissociation, and consequently accelerates and increases the reproduction of the decomposing substance. That this action is one dependent upon the mass and not the quality of the substance composing the atmosphere is shown by the fact that when equal volumes of the products of dissociation are produced, then it is of no importance which of the two products of dissociation constitutes the atmosphere surrounding the decomposing compound.[1] Thus the tension of dissociation of ammonium chloride is reduced to the same extent when decomposed in an atmosphere of equal volumes of either hydrochloric acid gas or ammonia. If, however, the products of dissociation are formed in unequal volumes, then an excess of one of the products will have a greater effect than an equal excess of the other. Ammonium carbamate dissociates into ammonia and carbon dioxide, thus:

$$NH_2COONH_4 = NH_3 + CO_2 + NH_3,$$

[1] A. Horstmann, *Ber. d. deut. chem. Ges.* 1876, ix. 1625.

and consequently an excess of ammonia lessens the dissociation to a greater extent than an equal volume of carbon dioxide. Since every two molecules of NH_3 require one molecule of CO_2 to reproduce ammonium carbamate, this must evidently take place more rapidly when every particle of CO_2 produced in the dissociation is surrounded by ammonia than when ammonia is surrounded by molecules of carbon dioxide.

§ 239. That in the commoner forms of chemical change, consisting of the double decomposition of two compounds, the mass of one of these exerts considerable influence, is a fact that has been recognised from an early period in applied chemistry. C. L. Berthollet[1] was the first to draw attention to the influence of mass, and to investigate the same from a theoretical point of view. Starting with the proposition that every action of a substance must increase with the amount of the active mass, he deduced laws for chemical changes, which he found, or convinced himself, were confirmed by many results of actual experiment. The law that, when two substances having an affinity for a third react simultaneously upon this substance, their action is not dependent alone upon the strength of their affinities but upon the mass of each taking part in the action, forms the basis of his theory. Berthollet therefore makes chemical action proportional to mass and to affinity.

Inasmuch as the results of the investigations of J. B. Richter, which formed the basis of stochiometry, were unknown to Berthollet, he, in company with many of his predecessors, more especially Bergmann, fell into the pardonable error of looking upon the power of saturation as affinity, and considered that the affinity might be measured by the amount of acid required to neutralise a given quantity of a base, and the smaller the amount of acid the greater the affinity. If the theories adopted at the present time be entirely disregarded, this view of the matter appears to be a very obvious one; but when considered from our present standpoint, it is at once evident that Berthollet, unwittingly,

[1] *Recherches sur les lois de l'Affinité*, Paris, an IX, reprinted from the *Mém de l'Institut*; *Essai de Statique chimique*, Paris, an XI (1803).

considered stochiometry alone, and left affinity quite out of the question.

His measure of chemical action was 'chemical mass,' that is to say, the product of the mass of the substance into the strength of its affinity. The latter he took as equivalent to the power of saturation, consequently inversely proportional to the equivalent weight. It follows, therefore, that his chemical mass represents nothing more than the quotient obtained by dividing the mass by the equivalent weight, or, in other words, the number of equivalents of the substance taking part in the change. Accordingly a substance, for instance a base, reacting simultaneously upon two other substances having an affinity for it, as, for instance, two acids, would combine with each of these in proportion to their respective equivalent weights. For example, an equivalent of soda, added to a mixture containing equivalent quantities of sulphuric and nitric acids, would neutralise the half of each of these acids. If, on the other hand, two equivalents of sulphuric acid and one equivalent of nitric acid react upon one equivalent of a base, then two-thirds of the equivalent of sulphuric, and only one-third of the equivalent of nitric acid will be neutralised, and consequently one-third of the equivalent of sulphuric, and two-thirds of the equivalent of nitric acid, will remain unaltered. Berthollet pointed out at the same time that the application of this law is frequently interfered with by the insolubility or volatility of the compounds produced in such chemical changes; he could not, however, with the limited knowledge of his time, recognise what at once occurs to us, that this law presupposes that the affinities of the equivalent weights of all acids are equal to one another, and consequently the true interpretation of the facts can only be attained by consideration of the differences of the affinities. But that this law required only slight alterations to become a complete and exact interpretation of facts speaks very highly for Berthollet's penetration.

This correction would probably have followed very quickly had not Berthollet, by what we at the present time know to be an incorrect deduction from his theoretical standpoint, placed himself in opposition to the laws of stochiometry, and

Dalton's atomic theory. He supposed that, when two bodies react upon one another, the result must be proportional to the masses taking part in the action, so that the compound formed will contain a larger amount of the substance present in the greater proportion. The discussion which arose out of this erroneous view had the effect of diverting the attention of chemists to other theories. Whilst his laws as to the influence of solubility, volatility, &c., have always received some consideration, the important doctrine of the influence of mass remained almost entirely forgotten for two generations.

§ 240. After Malaguti [1] had, by a method not altogether free from error, investigated the mutual decomposition of salts in solution, on lines similar to those laid down by Berthollet, Bunsen,[2] in 1853, by his investigation on 'Chemical Affinity,' again drew attention to Berthollet and his doctrines, demonstrating, as he did, experimentally, the influence exercised by mass in the distribution of oxygen among two combustible gases, hydrogen and carbon monoxide. Debus,[3] about the same time, and in connection with Berthollet's theory, studied the manner of distribution of carbon dioxide in aqueous solutions between baryta and lime, and also, in the same manner, A. Chižniski [4] afterwards investigated the distribution of phosphoric acid between lime and magnesia.

The investigations of Berthelot and Péan de Saint Gilles [5] on the formation of ethers from acids and alcohols, published in 1861 and 1862, have shown that in the province of organic chemistry the influence of mass is one of great importance. They have shown that when the proportion of the masses remains the same the final result is not affected, in whatever combination the substances are brought together, and that the final result is dependent to a greater extent upon the active masses, calculated according to the equivalents, than upon the intrinsic character of the substances and their affinities. They found, in the case of all the alcohols and acids studied

[1] *Ann. Chim. Phys.* [3] xxxvii. 198; also 1857, li. 328.
[2] *Liebig's Annalen*, 1853, lxxxv. 137.
[3] *Ibid.* 1853, lxxxv. 103, and lxxxvi. 156.
[4] *Ibid.* 1866, Suppl.-Bd. iv. 226.
[5] *Ann. Chim. Phys.* [3] 1862, lxv. 385; lxvi. 5.

by them,[1] and employed in equivalent proportions, that the etherification proceeded to the same extent in each.

§ 241. These observations show that Berthollet's doctrine in its original form is insufficient to explain completely the observed phenomena. In 1867 Guldberg and Waage,[2] by remodelling Berthollet's doctrine, provided a theory of the influence of mass in chemical changes, by the aid of which a large number of observations can be satisfactorily explained, and one which is, moreover, apparently capable of further development.

According to Berthollet the amount of a compound produced in a given chemical change is simply proportional to the number of equivalents of the substance present which tends to form it. If A be the equivalent of an acid, and B that of a base, whilst C represents the equivalent of a second acid, and further supposing p, q, r, represent respectively the equivalents of these substances reacting upon one another, then the base will be divided between the two acids in the proportion of

$$\frac{p}{p+r} \quad \text{to} \quad \frac{r}{p+r}$$

and consequently the formation of the salts AB and CB will take place as represented by the equation

$$pA + qB + rC =$$

$$\frac{pq}{p+r}\,AB + \frac{rq}{p+r}\,CB + \left(1 - \frac{pq}{p+r}\right)A + \left(1 - \frac{rq}{p+r}\right)C.$$

This result would only be interfered with by the insolubility or volatility of one of the compounds; the manner in which the phenomena are so affected will be presently explained.

Guldberg and Waage have introduced into this altogether too simple theory the influence exercised on the decomposition by time, space, temperature, and the strength of the affinities. Inasmuch as a body will react the more power-

[1] Menschutkin has shown this is not so generally true, but only true of bodies belonging to the same classes (*vide* § 244).

[2] *Etudes sur les Affinités chimiques, programme de l'université Christiania*, 1867. J. van 'tHoff has independently and without knowledge of this work proposed a similar theory (*Ber. d. deut. chem. Ges.* 1877, x. 669).

fully upon another the greater the mass of it coming in contact with this body, therefore the result of its action will be proportional to the quantity of the other substance brought within its sphere of action. But, inasmuch as the extent of the sphere of action is unknown to us, so Guldberg and Waage substitute for it the unit of space, and consider the quantity of a body contained in this unit of space as its active mass, which latter is conveniently taken as expressed by the number of equivalent weights contained in the unit of space. The interaction of several substances upon one another will therefore be proportional to the active masses of each, consequently to the products of all the active masses. Supposing the unit of volume to contain p equivalents of one substance, and q of another, then the following will be an expression of their action upon one another :—

$$k \cdot p \cdot q,$$

where k represents a number dependent upon the nature of the substances, the temperature, and other external conditions.

Whilst the deductions may, without special difficulty, be made from these suppositions, and represented by mathematical formulæ, it is, at the same time, in the majority of cases, extremely difficult to compare them with actual experience. As no direct measurement can be made of the strength of the forces coming into play, we must therefore be content to gather this from the forces themselves, from the range of their action, *i.e.* from the magnitude of the changes produced by them; this can, therefore, only be done by attempting to measure these quantities from a certain number of observations in which the results are dependent upon these, and then seeing whether these results explain satisfactorily other phenomena which are entirely or in part dependent upon the same causes.

Special care is therefore needed in the choice of the phenomena studied, in order to insure that the matters compared with one another are suitable for comparison.

§ 242. Guldberg and Waage have applied their theory to such decompositions as may be reversed, and therefore, as

a rule, remain incomplete. Such phenomena were chosen because they permitted of the possibility of comparing the forces favouring the reaction with those by which the reaction is hindered. It appears that this class of phenomena is much more numerous than was formerly supposed; so that by proving the truth of this theory, it is, at the same time, established that the theory may serve for the explanation of many, if not all, kinds of chemical changes.

If $$A + B' = A' + B$$

express a reversible reaction in which A is a compound which under the influence of B′ is converted into A′, whilst B′ is simultaneously converted into B, then $A' + B = A + B'$ represents the reverse reaction. To make the idea more real, the plain letters may be taken to represent acids, and the letters provided with a stroke their salts or ethers; or, the former may be considered as representing the oxidisable elements, whilst the latter represent their oxides. If both reactions can take place, then, in the majority of cases, they will do so side by side, and a state of equilibrium will be attained, in which all four compounds are present simultaneously. This equilibrium does not consist in an absence of activity, but is stationary to the extent only that exactly the same number of particles undergo decomposition in one direction as the number of particles undergoing decomposition in the opposite direction, so that the number of each species of substance remains unchanged. This number, as already described in § 194, is not alone dependent upon the strength of the affinities, but upon a whole series of external circumstances; it is in the last degree determined by the time required by each of these changes. If the quantities of the substances contained in the unit of space, or the 'active masses,' be

$$pA + qB + p'A' + q'B',$$

then the number of particles decomposed in one way will be

$$k\,p\,q',$$

whilst those decomposed in the reverse direction will be

$$k'\,p'\,q.$$

And the stationary state will be attained when

$$k\,p\,q' = k'\,p'\,q, \text{ or } k\frac{p}{q} = k'\,\frac{p'}{q'};$$

that is to say, when, in equal times, the changes taking place in one direction are equal to those taking place in the opposite direction.

The factors k and k' occurring in the above equations are styled 'coefficients of affinity' by Guldberg and Waage,[1] who have thus retained an expression introduced by Bunsen.[2] These factors have the very simple import that they give the proportions in which the substances A and B are converted into A′ and B′. If the proportion of the decomposed to the undecomposed number of equivalents, that is to say, the quotients

$$\frac{p'}{p} \quad \text{and} \quad \frac{q'}{q},$$

be styled the quotients of decomposition of the substances A and B, then from the above equation we have the following relation:—

$$\frac{p'}{p} : \frac{q'}{q} = k : k';$$

and therefore the proportion between the quotients of decomposition is constant, and is equal to the proportion between the coefficients of affinity.

Amongst the six unknown quantities occurring in this expression are p, p', q, q', which can be determined experimentally. If in any given case the values of these be known, then, although the coefficients of affinity themselves cannot be determined, still, their proportion to one another may be calculated.[3] If the experiment be so arranged that

$$p + p' = q + q' = p' + q' = 1,$$

which can be simply attained by bringing A and B′, or A′ and B together in the proportion of their equivalents (for example,

[1] *Etudes*, p. 7. [2] *Liebig's Annalen*, 1853, lxxxv. 154.

[3] Compare W. Ostwald, *Volumchemische Studien über Affinität*, Magister Dissertation, Dorpat, 1877, 17; *Journ. f. pr. Chem.* 1877, xvi. 391; 1879, xix. 471.

an equivalent of the acid A with an equivalent of the salt B'), then it follows that

$$p' = 1 - p = q,\ q' = 1 - q = p,$$

and the solution will contain in equilibrium

$$p\text{A} + (1 - p)\ \text{B} + (1 - p)\ \text{A}' + p\text{B}',$$

and therefore

$$\frac{k}{k'} = \left(\frac{1 - p}{p}\right)^2.$$

Inasmuch as k and k' cannot be singly determined, a single constant may be introduced in their place, which may be done by placing the quotient of k, by k' equal to x^2, from which it follows that

$$k : k' = x : \frac{1}{x};$$

x and $\frac{1}{x}$ are therefore in the same ratio as the coefficients of affinity, and by introducing x the following relation is obtained :—

$$x^2 = \left(\frac{1 - p}{p}\right)^2,\ x = \frac{1 - p}{p},\ p = \frac{1}{1 + x}.$$

And when this value for p is used, the following expression represents the condition of equilibrium :—

$$1\ \text{A} + x\ \text{B} + x\ \text{A}' + 1\ \text{B}',$$

or

$$\frac{1}{x}\text{A} + 1\ \text{B} + 1\ \text{A}' + \frac{1}{x}\text{B}',$$

which is, therefore, the proportion of the coefficient x to unity :

$$x : 1, \text{ or } 1 : x,$$

which will be attained when the opposing substances A and B pass into the condition represented by A' and B', as, for instance, when two acids combine with one base, all three reacting upon one another in equivalent quantities.

If this proportion of the distribution has been once determined for any given quantities of the active masses, then by its aid the condition of equilibrium of any other masses may

be calculated. If the theory be correct the following relations must always obtain:—

$$k\frac{p}{q} = k'\frac{p'}{q'}, \text{ or } \frac{p'}{p} : \frac{q'}{q} = k : k' = x : \frac{1}{x};$$

that is to say, the decomposition will proceed to such an extent that the relation between the coefficients of decomposition will be equal to the coefficients of affinity, whatever the quantities of materials used, provided only that all external conditions remain the same. If the amounts of each substance contained in the solution be experimentally determined, as, for instance, those of the two acids (P and Q), and of the base (R), then we have further relation:

$$P = p + p',\ Q = q + q',\ R = p' + q',$$

and thus obtain four equations for the determination of the four unknowns, p, p', q, and q'.

On the other hand, not only can P, Q, and R be so determined, but also the values of p, q, p', and q', and these may therefore be compared with those obtained from the above equations, and in this way the correctness of the theory so tested. This theory has already satisfactorily withstood similar tests.

§ 243. The observations of Berthollet and Péan de Saint Gilles on etherification, which have already been mentioned, are well adapted to show the validity of this theory. If we take

A = acetic acid = $C_2H_3O_2H$. B = water = HOH.

A′ = ethylacetate = $C_2H_3O_2C_2H_5$. B′ = alcohol = HOC_2H_5,

then the final state of equilibrium attained after some time is represented by the expression

$$p\,C_2H_4O_2 + p'\,C_4H_8O_2 + q\,H_2O + q'\,C_2H_6O,$$

in which, according to theory, the relation between the coefficients of decomposition and those of affinity must be the following:—

$$\frac{p}{p'} : \frac{q}{q'} = \frac{1}{x} : x \text{ or } \frac{p'q}{pq'} = x^2.$$

The investigations of these chemists in which the unaltered quantity of acid p was determined by titration, have shown, in the first place, that this condition of equilibrium is the same, whether the alcohol and acid react upon one another, or whether corresponding amounts of ether and water are brought together. The attainment of this equilibrium requires considerable time, and, in fact, the lower the temperature, the greater the length of time required.

If P mol.-wts. of acetic acid and Q mol.-wts. of alcohol are allowed to react upon one another, then, when x mol.-wts. of ethyl acetate and x mol.-wts. of water have been produced according to the equation

$$x\ C_2H_3O_2H + x\ HOC_2H_5 = x\ C_2H_3O_2C_2H_5 + x\ HOH,$$

the condition is

$$(P - x)C_2H_4O_2 + x\ C_4H_8O_2 + (Q - x)C_2H_6O + x\ H_2O.$$

If we express by ξ the extreme value assumed by x in the state of equilibrium, which is attained after some time, then we shall have

$$p = P - \xi,\ p' = q = \xi,\ q' = Q' - \xi.$$

In order to be able to calculate the value of ξ in every case, the value of the coefficient of affinity x must be determined first, for which an experimental determination of ξ in any single given case will suffice.

When $P = Q'$, it was found $p = 0{\cdot}335\ P$, from which

$$p' = q = \xi = 0{\cdot}665\ P,\ q' = 0{\cdot}335\ P,$$

$$x^2 = \frac{p'q}{pq'} = \left(\frac{\xi}{1 - \xi}\right)^2 = 3{\cdot}94,\ x = \frac{\xi}{1 - \xi} = 1{\cdot}985.$$

Or, in round numbers,

$$x^2 = 4,\quad x = 2.$$

Consequently, when the same number of equivalents of acid and alcohol are used, the proportion of acid converted into ether to the unaltered acid is as 2 : 1.

If from the commencement we have not only acid and alcohol present, but also P′ mol.-wts. of the ether, and Q

mol.-wts. of water, then for the condition of equilibrium we have the following expressions:—

$$p = (P - \xi),\ p' = (P' + \xi),\ q = (Q + \xi),\ q' = (Q' - \xi),$$

and by substituting these values in the equation for x^2, the following is obtained:—

$$x^2 = \frac{(P' + \xi)(Q + \xi)}{(P - \xi)(Q' - \xi)},$$

which gives the following value for ξ:—

$$\xi = \frac{x^2(P + Q') + (P' + Q)}{2(x^2 - 1)} \pm \sqrt{\left(\frac{x^2(P + Q') + (P' + Q)}{2(x^2 - 1)}\right)^2 + \frac{P'Q - x^2PQ'}{x^2 - 1}},$$

in which, when $x^2 > 1$, the minus sign must be used, and the plus sign when $x^2 < 1$. When $x^2 = 4$ we have the following expression for ξ:—

$$\xi = \frac{4P + 4Q' + P' + Q}{6} - \sqrt{\left(\frac{4P + 4Q' + P' + Q}{6}\right)^2 + \frac{P'Q + 4PQ'}{3}}.$$

To test the validity of the theory, the values of ξ may be calculated by the aid of this formula, and these compared with those deduced from observation. In the following table the observed and calculated values are placed side by side. Further, x^2 can be deduced from individual observations, and these values are to be found in the last column but one.

Acid P	Alcohol Q'	Ether P'	Water Q	ξ obs.	ξ calc.	x^2	Δx^2
1	1	0	0	0·665	0·667	3·94	+0·21
1	2	0	0	0·828	0·845	3·40	−0·33
1	4	0	0	0·902	0·930	2·68	−1·05
2	1	0	0	0·858	0·845	3·61	−0·12
1	1	1·6	0	0·521	0·492	4·82	+1·09
1	1	0	3	0·407	0·409	3·96	+0·23
1	1	0	23	0·116	0·131	3·43	−0·30
1	2	0	98	0·073	0·073	4·01	+0·28
					Mean	3·73	

Considering the difficulties surrounding these observations, the agreement between the observed and calculated values for ξ is sufficiently satisfactory.

The values for x^2 are not, as required by theory, identical, but the differences from the mean (Δx^2) are quite irregular, at one time in one direction, at another time in the opposite, and are probably due to experimental errors. Since, from the character of the experimental determination of p, the value of ξ will probably be found too small rather than too large, and therefore the mean of x^2 is also probably too small, so the above expression $x^2 = 4$ is most probably the correct one.

Observation, therefore, supports the theory of Guldberg and Waage. Accordingly the formation of ethyl acetate from acetic acid and alcohol proceeds until the proportion between the etherified to the unaltered acid is equal to four times the proportion between the number of the molecules of the unaltered alcohol and the number of the molecules of water.

§ 244. Menschutkin [1] has supplemented the researches of Berthollet and Péau de Saint Gilles by investigating the rate and the limit of etherification of different kinds of alcohols by acetic acid, and he has found that both these values are almost equal for alcohols of the same class, but are very different for different classes of alcohols. The primary saturated alcohols (see § 135), $C_nH_{2n+2}O$, are most rapidly and most completely etherified, the only difference being that the lower members of the series, which are soluble in water, are more rapidly, but less completely, etherified than the higher members which are insoluble in water and form ethereal salts which are less easily decomposed by water than the corresponding compounds of the lower alcohols. The primary non-saturated alcohols come next in order, then the secondary saturated alcohols, followed by the secondary non-saturated alcohols. Finally we have the tertiary alcohols, with a very low rate of etherification. The 'limit' cannot be accurately determined, since the ethereal salts decompose, forming hydrocarbons. The phenols, of which the rate and limit of etherification have been determined, resemble the tertiary alcohols.

Menschutkin's results are contained in the following table.

[1] *Liebig's Ann.* 1879, cxcv. 334; cxcvii. 193.

In these experiments P = Q′; the temperature is 154° unless otherwise stated. The limits of etherification attained in 120 hours are given under ξ, and also the values x^2 and x, calculated from these data. The initial rate of etherification, *i.e.* the proportion of acid or alcohol etherified during the first hour, is given under *G*.

	M	G	ξ	x	x^2
I. Primary Alcohols.					
a. Saturated—					
Methyl alcohol	CH_4O	0·556	0·696	2·29	5·24
Ethyl alcohol	C_2H_6O	0·469	0·666	2·00	4·00
Norm. Propyl alcohol	C_3H_8O	0·469	0·668	2·01	4·05
,, Butyl alcohol	$C_4H_{10}O$	0·469	0·673	2·06	4·24
Isobutyl alcohol	,,	0·449	0·674	2·07	4·28
Norm. Octyl alcohol	$C_8H_{18}O$	0·466	0·723	2·61	6·81
Cetyl alcohol	$C_{16}H_{34}O$	—	0·804	4·10	16·83
b. Non-saturated—					
Allyl alcohol	C_3H_6O	0·361	0·594	1·46	2·14
Benzyl alcohol	C_7H_8O	0·386	0·608	1·55	2·41
II. Secondary Alcohols.					
a. Saturated—					
Dimethyl carbinol	C_3H_8O	0·277	0·605	1·53	2·35
Ethylmethyl carbinol	$C_4H_{10}O$	0·226	0·593	1·46	2·12
Isopropylmethyl carbinol	$C_5H_{12}O$	0·189	0·593	1·46	2·12
Diethyl carbinol	,,	0·169	0·587	1·42	2·02
Hexylmethyl carbinol	$C_9H_{20}O$	0·212	0·620	1·63	2·66
b. Non-saturated—					
Ethylvinyl carbinol	$C_5H_{10}O$	0·149	0·523	1·07	1·20
Diallyl carbinol	$C_7H_{12}O$	0·103	0·501	1·02	1·01
III. Tertiary Alcohols.					
a. Saturated—					
Trimethyl carbinol	$C_4H_{10}O$	0·022	0·071[1]		
Ethyldimethyl carbinol	$C_5H_{12}O$	0·012	0·034		
Diethylmethyl carbinol	$C_6H_{14}O$	0·018	0·019		
Propyldimethyl carbinol	,,	0·021	—		
Isopropyldimethyl carbinol	,,	0·009	0·016		
b. Non-saturated—					
Allyldimethyl carbinol	$C_6H_{12}O$	0·038	0·075		
Allyldiethyl carbinol	$C_9H_{16}O$	0·000	0·034		
Allyldipropyl carbinol	$C_{12}H_{24}O$	0·000	0·006		
Diallylmethyl carbinol	$C_9H_{14}O$	0·000	0·003		
Diallylpropyl carbinol	$C_{12}H_{18}O$	0·000	0·003		
IV. Phenols.					
Phenol	C_6H_6O	0·018	0·090	0·099	0·0098
Paracresol	C_7H_8O	0·018	0·097	0·107	0·0115
Thymol	$C_{10}H_{14}O$	0·058	0·095	0·105	0·0110
a Naphthol	$C_{10}H_8O$	—	0·063	0·067	0·0045

[1] At 100° ξ = 0·123.

If we examine the numbers in the preceding table (not forgetting to take into account the arrangement of the atoms in these different classes of alcohols, *vide* § 132), we find that the more H atoms there are attached to the C atom, which is united to the OH group, the more rapid and the more complete the process of etherification will be. On the other hand, it diminishes with the number of C atoms directly attached to this C atom. But, at the same time, the miscibility of the alcohol and its ether in water exerts an undeniable influence on these values. It is obvious that, when ξ is very small, the value of x is only approximately correct.

Menschutkin [1] has also determined the velocity and the limits of etherification of ethyl and isobutyl alcohols for different acids at 154°. In the following table the numbers obtained with ethyl alcohol are distinguished by an asterisk. They show that etherification is more rapid, but not, as a rule, so complete in the case of ethyl alcohol as it is for isobutyl alcohol.

	M	G	ξ	x	x^2
a. Primary acids [2]—					
Formic acid [3] . . .	CH_2O_2	0·617	0·642	1·79	3·22
Acetic „ . . .	$C_2H_4O_2$	0·444	0·674	2·07	4·28
„ „ . . .	„	0·470*	0·666*	2·00*	4·00*
Propionic „ . . .	$C_3H_6O_2$	0·412	0·687	2·20	4·82
Norm. Butyric acid . .	$C_4H_8O_2$	0·333	0·695	2·28	5·19
„ „ „ . .	„	0·360*	0·688*	2·21*	4·86*
„ Caproic „ . .	$C_6H_{12}O_2$	0·331	0·698	2·31	5·34
„ „ „ . .	„	0·346*	0·698*	2·31*	5·34*
„ Octylic „ . .	$C_8H_{16}O_2$	0·309	0·709	2·44	5·94
b. Secondary acids—					
Isobutyric acid . . .	$C_4H_8O_2$	0·290	0·695	2·28	5·19
Methylethylacetic acid .	$C_5H_{10}O_2$	0·215	0·737	2·80	7·85
c. Tertiary acids—					
Trimethylacetic acid . .	$C_5H_{10}O_2$	0·083	0·727	2·66	7·09
Dimethylethylacetic acid .	$C_6H_{12}O_2$	0·035	0·742	2·88	8·27
„ „ .	„	0·054*	0·739*	2·83*	8·02*
Heptylic acid [4] . . .	$C_7H_{14}O_2$	0·004	—	—	—
Decylic [4] „ . . .	$C_{10}H_{20}O_2$	0·005	—	—	—

[1] *Ber. d. deut. chem. Ges.* 1879, 2168.

[2] Acids are termed primary, secondary, or tertiary, respectively, when the position of their carboxyl group, COOH, is identical with that of the hydroxyl OH in the primary, secondary, or tertiary alcohols.

[3] At 100°, since the acid decomposes at a higher temperature.

[4] The constitution of these acids has not yet been thoroughly investigated.

There is a considerable difference between the primary, secondary, and tertiary acids. The rate of etherification diminishes in passing from the primary to the secondary acids, and again from the secondary to the tertiary; but, on the other hand, the limit of etherification increases.

The same author has obtained similar results for non-saturated acids of different constitutions, and also for polyvalent alcohols and phenols.[1] By numerous systematic investigations he has succeeded in deriving from the rate and limit of etherification a valuable means of distinguishing between differently constituted alcohols and acids.

§ 245. When two acids act upon one base, which is not present in sufficient quantity to saturate them both completely, the manner in which the two acids are divided between the base cannot be ascertained by analysis if all the resulting products remain in solution, but it can be calculated from various phenomena accompanying the reaction. For this purpose Julius Thomsen has made use of the heat developed on mixing dilute solutions of these bodies.[2] He started from the following hypothesis: 'Different acids, on neutralisation with the same base, evolve different amounts of heat; if one acid replaces another from its compound with the base, the decomposition of the salt is accompanied by a thermic change in which heat is evolved or absorbed, according as the heat of neutralisation of the free acid is greater or less than that of the acid contained in the salt.

'The extent of the decomposition can be determined from the value of the thermic effect.'

But for this determination it is necessary to make an extensive series of experiments, showing the thermochemical effect of each pair of the substances in question.

The action of each acid on the base must be separately determined, then the action of each acid on its own salt, and also on the salt of the other acid, and, finally, the mutual action of the two acids. These experiments were generally

[1] *Ber. d. deut. chem. Ges.* 1880, 162, 163, 1812, 1814. Complete résumé, *Ann. Chim. Phys.* [5] 1880, xx. 289.

[2] On Berthollet's 'Theory of Affinity,' *Pogg. Ann.* 1869, cxxxviii. 65–102, *Therm. Untersuchung*, i. 97, &c.

made with different weights of the substances. The quantity of water serving as solvent varied but slightly, so that the results of the experiments only held good for dilute solutions.

The greatest possible care has to be exercised in each individual determination, in order that the result may be trustworthy; if due caution is not observed utterly false results are easily obtained.

Let A and B represent the equivalent weights of the two acids, and A′ and B′ those of their salts; then the solution will contain in a state of equilibrium the quantities

$$p\,.\,\mathrm{A} + p'\,\mathrm{A}' + q\mathrm{B} + q'\mathrm{B}',$$

and
$$x\,\frac{p}{p'} = \frac{1}{x}\,\frac{q}{q'} \text{ or } x^2 = \frac{p'\,.\,q}{p\,.\,q'} = \text{constant}.$$

If the four substances are mixed in these proportions, no thermic effect is produced, but if mixed in any other proportion, the decomposition required to bring about a state of equilibrium is accompanied by a thermic effect.

In order to determine the constants x^2, Thomsen investigated the two simplest cases where 1 equivalent A acts on 1 equivalent B′, and 1 equivalent B acts on 1 equivalent A′. In these cases we have

$$p + p' = 1,\ q + q' = 1,\ p' + q' = 1,$$

and for the state of equilibrium (*vide* § 242)

$$p\mathrm{A} + (1-p)\,\mathrm{A}' + (1-p)\,\mathrm{B} + p\mathrm{B}',$$

or
$$\mathrm{A} + x\mathrm{A}' + x\mathrm{B} + \mathrm{B}'.$$

If the heat of neutralisation, *i.e.* the thermic effect, of the complete neutralisation of an equivalent of each of the acids is W(A) and W(B), then the partial exchange of the base on mixing 1 A with 1 B′ produces the thermic effect

$$(\mathrm{A} : \mathrm{B}') = (1-p)\,(\mathrm{W(A)} - (\mathrm{W(B)});$$

but on mixing 1 B with 1 A′ the thermic effect is

$$(\mathrm{B} : \mathrm{A}') = p\,(\mathrm{W(B)} - \mathrm{W(A)});$$

for, in the first case $(1-p)$ equivalents of the salt A′, in the second p equivalents of the salt B′ are formed. On the other

hand, in the first case $(1 - p)$ equivalents of the acid B, in the second p equivalents of the acid A are set at liberty, and consequently their heat of neutralisation is used up, and must be represented as a negative quantity in the calculation.

Secondary thermic effects are also produced by the mutual action of the other bodies. According to Thomsen's experiments, although the action of one acid on the other and the action of the salts on each other do not produce any effect capable of measurement, still, each acid produces a greater or less thermic effect with its own salt.

These secondary reactions are, however, the same in each case, since they depend entirely on the quantities of acids and salts produced; in the first case $(1 - p)$ A′ is formed, which acts on pA, and $(1 - p)$ B which acts on pB′. In the second case pA is formed, and acts on the remaining $(1 - p)$ A′, and pB′ acting on $(1 - p)$ B.

The complete thermic effect on mixing 1 A and 1 B′ is, therefore,

$$(A : B') = (1 - p)\ (W(A) - W(B)) + ((1 - p)\ A', pA) + ((1 - p)\ B, pB'),$$

and on mixing 1 A′ and 1 B,

$$(B : A') = p\ (W(B) - W(A)) + (pA\ (1 - p)\ A') + (pB'\ (1 - p)\ B).$$

According to the general laws of the mechanical theory of heat, the calorific effect depends only on the initial and final state of a system, and not on the order in which the change takes place. Hence it follows that

$$(A : B') - (B : A') = W(A) - W(B).$$

This also follows from the preceding equation. Thomsen found for

$A = \frac{1}{2} H_2SO_4$, $A' = \frac{1}{2} Na_2SO_4$, $B = HNO_3$, $B' = NaNO_3$.

$(A : B') - (B : A') = +288$ cal. $- (-1752^c) = 2040^c$.

$W(A) - W(B) = 15689^c - 13617^c = 2072^c$.

and for

$A = \frac{1}{2} H_2SO_4$, $A' = \frac{1}{2} Na_2SO_4$, $B = HCl$, $B' = NaCl$.

$(A : B') - (B : A') = 244^c - (-1682^c) = 1926^c$.

$W(A) - W(B) = 15689^c - 13740^c = 1949^c$.

Theory and observation therefore agree very closely, with the exception of small deviations arising from the unavoidable errors of experiment.

§ 246. If we replace the values determined by experiment

$$(A : B') = 288^c, (B : A') = -1752^c, \text{ for } B = HNO_3,$$

and

$$(A : B') = 244^c, (B : A') = -1682^c, \text{ for } B = HCl,$$

in the above equation, p cannot be directly determined, since the values in the second and third brackets of the expressions for $(A : B')$ and $(B : A')$ vary with p.

Thomsen found

$$\tfrac{1}{2}\,(Na_2SO_4 : n\,H_2SO_4) = -\frac{n}{n + 0{\cdot}8} \cdot 1650^c.$$

$$(NaNO_3 : HNO_3) = -36^c : (NaCl, HCl) = -32^c.$$

The thermic effect of $\frac{p}{2}\,H_2SO_4$ and $\frac{1-p}{2}\,Na_2SO_4$ is

$$\frac{1-p}{2}\left(Na_2SO_4 : \frac{p\,H_2SO_4}{1-p}\right) = -\frac{p\,(1-p)}{0{\cdot}2\,p + 0{\cdot}8} \cdot 1650^c.$$

Assuming that the thermic effect of the corresponding quantities of both the other acids and their salts is proportional to the quantity of the free acid (an assumption which is permissible as the quantities are very small),

$$p\,(NaNO_3 : (1-p)\,HNO_3) = -(1-p)\,36^c$$

and

$$p\,(NaCl : (1-p)\,HCl) = -(1-p)\,32^c.$$

The value of p can now be determined from the equations [a] for sulphuric and nitric acids:

$$(A : B')^a = (1-p) \cdot 2072^c - \frac{p\,(1-p)}{0{\cdot}2 \cdot p + 0{\cdot}8} \cdot 1650^c.$$

$$-(1-p) \cdot 36^c = 288^c.$$

$$(B : A')^a = -p \cdot 2072^c - \frac{p\,(1-p)}{0{\cdot}2 \cdot p + 0{\cdot}8} \cdot 1650.$$

$$-(1-p)\,36 = -1752^c.$$

and (^{b}) for sulphuric and hydrochloric acids :

$$(A : B')^b = (1-p)^c\,1949 . - \frac{(p\,1-p)}{0{\cdot}2 . p + 0{\cdot}8} . 1650.$$
$$- (1-p) . 32^c = 244^c.$$

$$(B : A')^b = - p . 1949 - \frac{(p\,1-p)}{0{\cdot}2 . p + 0{\cdot}8} . 1650.$$
$$- (1-p) . 32^c = - 1682^c.$$

Thomsen solved this equation by trying different values for p, and neglecting the third number, which is very small. He found that $p = \frac{2}{3}$ satisfies both cases.

The calculated and observed values of p are :—

	Observed	Calculated	Difference
$(A : B')^a$	288 ^{c}	286 ^{c}	− 2 ^{c}
$(A : B')^b$	244	244	0
$(B : A')^a$	−1752	−1786	−34
$(B : A')^b$	−1682	−1703	−21

The calculated and observed results only exhibit very minute deviations. By replacing the value of p we obtain for the state of equilibrium

$$\tfrac{2}{3} . \tfrac{1}{2}\,H_2SO_4 + \tfrac{1}{3} . \tfrac{1}{2}\,Na_2SO_4 + \tfrac{1}{3}\,HNO_3 + \tfrac{2}{3}\,NaNO_3,$$
$$\tfrac{2}{3} . \tfrac{1}{2}\,H_2SO_4 + \tfrac{1}{3} . \tfrac{1}{2}\,Na_2SO_4 + \tfrac{1}{3}\,HCl + \tfrac{2}{3}\,NaCl,$$

and with whole coefficients

$$2\,H_2SO_4 + Na_2SO_4 + 2\,HNO_3 + 4\,NaNO_3,$$
$$2\,H_2SO_4 + Na_2SO_4 + 2\,HCl + 4\,NaCl,$$

or, if an acid sulphate is formed,

$$H_2SO_4 + 2\,HNaSO_4 + 2\,HNO_3 + 4\,NaNO_3,$$
$$H_2SO_4 + 2\,HNaSO_4 + 2\,HCl + 4\,NaCl.$$

On mixing a dilute solution of one equivalent of each acid with one equivalent of soda, the acids are divided between the base as follows : one-third of the sulphuric, and two-thirds of the nitric or hydrochloric acids are saturated.

In order to determine the constant x we have

$$x^2 = \left(\frac{1-p}{p}\right)^2 = \tfrac{1}{4}, \quad x = \tfrac{1}{2}, \quad \frac{1}{x} = 2.$$

If we replace this value for x, in the general equation, we have

$$x^2 = \frac{p' \cdot q}{p \cdot q'} = \tfrac{1}{4}, \quad \frac{1}{x^2} = \frac{p \cdot q'}{p' \cdot q} = 4.$$

and $$\frac{p}{p'} = 4\frac{q}{q'}, \quad \text{or} \quad \tfrac{1}{2}\frac{p}{p'} = 2\frac{q}{q'}.^1$$

This may be expressed in words as follows:

When nitric or hydrochloric acid and sulphuric acid are mixed with a dilute solution of a base in insufficient quantity for their complete saturation, the ratio of the unsaturated equivalents of the sulphuric acid to the equivalents of the saturated acid is always four times the ratio which the non-saturated equivalents of hydrochloric or nitric acid bears to the saturated equivalents.

If the preceding equation is written $\frac{1}{4}\frac{p}{q} = \frac{p'}{q'}$, its meaning may be expressed in words thus:

The ratio of the equivalents of sulphate to those of the nitrate is only $\frac{1}{4}$ of that of the free acids to each other.

§ 247. If P equivalents of sulphuric acid, and Q equivalents of nitric or hydrochloric acid are mixed with 1 equivalent of caustic soda in dilute solution, the four conditions for the state of equilibrium

$$p\,\tfrac{1}{2}\,H_2SO_4 + p'\,\tfrac{1}{2}\,Na_2SO_4 + q\,HNO_3 + q'\,NaNO_3,$$

are $$\frac{p}{p'} = 4\frac{q}{q'},\ p' + q' = 1,\ p + p' = P,\ q + q' = Q.$$

From which the equivalents of neutralised sulphuric acid may be calculated to be

$$p' = -\tfrac{1}{6}(4Q + P - 3)\sqrt{\tfrac{1}{3}P + [\tfrac{1}{6}(4Q + P - 3)]^2}.$$

In order to test the theory Thomsen made a large series of experiments, in which he determined the thermic effect produced by mixing different quantities of the acids and their salts, and he compared these results with those values calculated from the above or analogous formulæ.

[1] Thomsen gives the value as $\frac{1}{2}$, *Pogg. Ann.* cxxxviii. 90; also as 0·49, *ibid.* 498, and also as 0·515, *ibid.* 507. More recently he adheres to the number 0·49. As the true value has not been accurately ascertained, it is here taken as 0·5.

The first four columns of the following table contain the quantities of the different substances (expressed in equivalents) which are mixed together. The fifth and sixth columns contain the calculated and the experimental values of the thermic effect, and the last column shows the difference between these values.

$\frac{1}{2}H_2SO_4$	$\frac{1}{2}Na_2SO_4$	HNO_3	$NaNO_3$	Thermic effects		Difference
				calculated	found	
0	1	$\frac{1}{2}$	0	− 462°	− 452°	−10°
0	1	1	0	− 828	− 808	−20
0	1	$\frac{3}{2}$	0	−1331	−1292	−39
0	1	1	0	−1773	−1752	−21
0	1	2	0	−1974	−2026	+52
0	1	3	0	−2019	−2050	+31
1	1	2	0	− 982	− 978	− 4
2	1	2	0	− 714	− 664	−50
3	1	2	0	− 551	− 520	−31
0	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	− 561	− 546	−15
0	$\frac{1}{2}$	1	$\frac{1}{2}$	− 786	− 761	−25
0	$\frac{1}{2}$	1	$\frac{1}{2}$	− 933	− 968	+35
1	0	0	1	+ 298	+ 288	+10
2	0	0	1	+ 348	+ 379	−31
		HCl	*NaCl*			
0	1	$\frac{1}{2}$	0	−1279	−1247	−32
0	1	1	0	−1691	−1682	− 9
0	1	2	0	−1870	−1878	+ 8
0	1	4	0	−1917	−1896	−21
1	0	0	1	+ 257	+ 244	+13
2	0	0	1	+ 292	+ 336	−44

In these determinations a unit of heat corresponds to about 0·001° C., and the greatest deviation between the calculated and observed results is only 0·05° C. The close agreement exhibited in this table shows that Guldberg and Waage's rule is applicable in this case.

§ 248. By means of this rule, which has been thoroughly tested by experiment, we can calculate the distribution of the base between any given quantities of the two acids.[1]

The following table shows how many equivalents of sulphuric acid (p'), and how many equivalents of nitric acid ($1 - p'$) are neutralised by soda, when P equivalents of sulphuric acid, and Q equivalents of nitric acid are present to 1 equivalent of the base.

[1] For a graphic representation of these values, see Van t'Hoff, *Ber. d. deut. chem. Ges.* 1877, 673.

	p' (neutralised equivalents of sulphuric acid)					
For	P = 1	2	3	4	5	6
Q =						
1	0·33	0·46	0·54	0·59	0·63	0·67
2	0·16	0·26	0·33	0·39	0·44	0·48
3	0·10	0·17	0·24	0·29	0·33	0·37
4	0·07	0·13	0·18	0·23	0·27	0·30
5	0·05	0·10	0·15	0·19	0·22	0·25
6	0·04	0·09	0·12	0·16	0·19	0·22

	$(1-p')$ (neutralised equivalents of nitric acid)					
For	P = 1	2	3	4	5	6
Q =						
1	0·67	0·54	0·46	0·41	0·37	0·33
2	0·84	0·74	0·67	0·61	0·56	0·52
3	0·92	0·83	0·76	0·71	0·67	0·63
4	0·93	0·87	0·82	0·77	0·73	0·70
5	0·95	0·90	0·85	0·81	0·78	0·75
6	0·95	0·91	0·88	0·84	0·81	0·78

These numbers show that only relatively small quantities of sulphates can exist in dilute solutions in the presence of excess of nitric acid. They also show that not only does the ratio of one acid to the other influence the results, but also the proportion which the base bears to the two acids exerts a marked influence, *e.g.*:

For equal equivalents of the two acids, the amount of sulphate produced is diminished by increasing the excess of free acids.

When P = Q = 1, one-third of the base combines with the sulphuric acid, but if P = Q = 5, only a little more than one-fifth of the base unites with the sulphuric acid.

In order to effect a definite division of the base between the acids, the latter must be employed in the proportions indicated by the equations

$$P = \frac{p'}{1-p'}(x^2 Q - (1-p')(x^2-1)) = \frac{p'}{1-p'}[4Q - 3(1-p')],$$

$$Q = \frac{1-p'}{x^2 p'}(P + p(x^2-1)) = \frac{1-p'}{4p'}(P + 3p').$$

For example, if we wish the sulphuric acid to unite with the fractions of 1 equivalent of soda, given under p' in the

first column of the following table, when the solution contains Q = 1, 2, 3, &c. equivalents of nitric acid, it is necessary that the number of equivalents of sulphuric acid indicated in that portion of the table should be present in the solution.

The additional quantity of sulphuric acid required increases much more rapidly than that of the nitric acid. Thus, in order that the former should neutralise one-third, and the latter two-thirds of the base, we must take 1 equivalent of sulphuric acid to 1 of nitric, but for 2 equivalents of nitric acid three of sulphuric are required, for three, five equivalents, finally, for n equivalents of nitric acid, $2n - 1$ equivalents of sulphuric acid.

Two equivalents of sulphuric acid suffice in any case to convert $\frac{1}{3}$ of an equivalent of the base into sulphate.

In order that the base may be equally divided between the two acids, P must equal $4 . Q - 1{\cdot}5$, *i.e.* the equivalents of sulphuric acid must be $1\frac{1}{2}$ less than four times the number of equivalents of nitric acid.

	$P = \frac{p'}{1-p'}(4Q-3(1-p'))$					
p'	P	$Q=1$	2	3	4	5
0·1	0·444 $Q-0{\cdot}3$ =	0·14	0·59	1·03	1·48	1·92
0·2	$Q-0{\cdot}6$ =	0·4	1·4	2·4	3·4	4·4
0·25	1·333 $Q-0{\cdot}75$ =	0·58	1·92	3·25	4·58	5·92
0·3	1·714 $Q-0{\cdot}9$ =	0·81	2·53	4·24	5·96	7·67
0·333	2 . $Q-1$ =	1	3	5	7	9
0·4	2·667 $Q-1{\cdot}2$ =	1·47	4·13	6·80	9·47	12·13
0·5	4 . $Q-1{\cdot}5$ =	2·5	6·5	10·5	14·5	18·5
0·6	6 . $Q-1{\cdot}8$ =	4·2	10·2	16·2	22·2	28·2
0·667	8 . $Q-2$ =	6	14	22	30	38
0·7	9·333 $Q-2{\cdot}1$ =	7·23	16·57	25·90	35·23	44·57
0·75	12 . $Q-2{\cdot}25$ =	9·75	21·75	33·75	45·75	57·75
0·8	16 . $Q-2{\cdot}4$ =	13·6	29·6	45·6	61·6	77·6
0·9	36 . $Q-2{\cdot}7$ =	33·3	69·3	105·3	141·3	177·3
1·0	$P=\infty$	—	—	—	—	—

§ 249. J. Thomsen [1] introduced a name for the coefficient of affinity, x, which was in the first instance applied only to acids and bases. According to § 242, when two acids, present in equivalent proportions, are mixed with one equivalent of the base, they unite with the base in the proportion of $x : 1$.

[1] *Pogg. Ann.* 1869, cxxxviii. 90; *vide* also *Thermochem. Untersuchungen*, i. 115.

Thomsen has designated this value x by the term *avidity*, which he defines as 'the striving of an acid after neutralisation.' Berthelot[1] denies the necessity of introducing this term; but as the idea is directly based on the observed behaviour of bodies, his strictures are unfounded.

If, in working with equivalent quantities, one acid receives less of the base than the other, its capacity of combining with the base is smaller, and Thomsen's 'avidity' is the simplest measure of this property. It is obviously only a relative, and not an absolute measure, since the avidity of one acid can only be compared with that of another. Thomsen has chosen nitric acid as the unit, since it possesses the highest avidity which has been observed up to the present. The value of the avidity of all other acids is represented by fractions, *e.g.*

$$\text{Sulphuric acid, Av. } (\tfrac{1}{2}\,H_2SO_4) = \frac{1}{x} = \tfrac{1}{2}.$$

and so on, for each of the other acids.

Although there is no doubt that the notion of avidity is justified by observed facts, the question remains whether this new expression should be retained. It is only desirable to retain it so long as the old term 'affinity,' which is used by Guldberg and Waage, Ostwald, and other investigators to denote this force, is employed by other authors to denote a hypothetical value (mentioned in § 223) proportional to the heat of neutralisation, which is not in any way a measure of affinity.

The heat of neutralisation of sulphuric acid ($\frac{1}{2}\,H_2SO_4Aq$, NaOHAq) = 15689 ^{c}, and of nitric acid, (HNO_3Aq, NaOHAq) = 13617 ^{c}, are inversely as the actual affinities or avidities; for the heat of neutralisation of sulphuric acid is 15 % greater than that of nitric acid, whilst its affinity or avidity is only half that of nitric acid.

The heat of neutralisation is not in any way adapted to be a measure of affinity. But since it does happen to be regarded as a measure of affinity, it will be advisable to retain the name avidity so long as this misuse continues, and afterwards replace it by the old term affinity.

[1] *Essai de Mécanique chimique*, ii. 640.

§ 250. Thomsen has experimentally determined the avidity, *i.e.* $\frac{1}{x}$ of a large number of acids, and has obtained very different results for different acids. As a rule, the avidity of a given acid is independent of the nature of the base it neutralises, but Thomsen found that the avidity of sulphuric acid varies with the nature of the base. Taking the avidity of hydrochloric acid as the standard,[1] the avidity of sulphuric acid is for

2NaOH	2KOH	$2NH_3$	MgO_2H_2	MnO_2H_2	ZnO_2H_2
0·50	0·57	0·56	0·69	0·71	0·73
	FeO_2H_2	CoO_2H_2	NiO_2H_2	CuO_2H_2	
	0·75	0·77	0·78	0·81	

Thomsen has generally determined the avidity for the equivalent weight of the acid, *i.e.* in the case when one equivalent of each of the two acids experimented on acts on one equivalent of the base (generally 1 NaOH). But he has made an exception in the case of certain polybasic acids, such as the phosphoric acids,[2] which unite with the different equivalents of soda required for their neutralisation with unequal force. In such cases he has used molecular instead of equivalent weights.

In order to obtain numbers comparable in every respect, it is advisable to determine the avidity of all polybasic acids for equivalent and also for molecular weights. These values can easily be calculated from each other. If $\mathfrak{M} = n$. Eq, *i.e.* if the molecular weight is n times the equivalent weight, the value of p' is deduced from the equation in § 247, in which we set $P = n$ and $Q = 1$, and this value $\mathfrak{p}$ is introduced into the equation in § 249 for the avidity,

$$(Av) = \frac{1}{x}.$$

Then, since $Q - 1 = 0$,

$$\mathfrak{p} = \frac{-(n+1) + \sqrt{4x^2n + (n-1)^2}}{2(x^2-1)},$$

and for the molecular avidity,

$$(Av)_M = \frac{\mathfrak{p}}{1-\mathfrak{p}} = \frac{-(n+1) + \sqrt{4x^2n + (n-1)^2}}{2x^2 + n - 1 - \sqrt{4x^2n + (n-1)^2}},$$

[1] *Thermochem. Unters.* i. 143. [2] *Pogg. Ann.* 1870, cxl. 94 and 505.

or, if the avidity of the equivalent $\frac{1}{x} = (\mathrm{Av})_{\mathrm{A}} = \mathrm{A}$ replaces x^2, then

$$(\mathrm{Av})_{\mathrm{M}} = \frac{-(n+1)\,\mathrm{A}^2 + \mathrm{A}\sqrt{4n + (n-1)^2\mathrm{A}^2}}{2 + (n-1)\,\mathrm{A}^2 - \mathrm{A}\sqrt{4n + (n-1)^2\,\mathrm{A}^2}},$$

and for the special cases,

$$n = 2 \quad (\mathrm{Av})_{\mathrm{M}} = \frac{-3\mathrm{A}^2 + \mathrm{A}\sqrt{8 + \mathrm{A}^2}}{2 - \mathrm{A}\sqrt{8 + \mathrm{A}^2}}$$

$$n = 3 \quad (\mathrm{Av})_{\mathrm{M}} = \frac{-4\mathrm{A}^2 + \mathrm{A}\sqrt{12 + 4\mathrm{A}^2}}{2 - \mathrm{A}\sqrt{12 + 4\mathrm{A}^2}}$$

$$n = 4 \quad (\mathrm{Av})_{\mathrm{M}} = \frac{-5\mathrm{A}^2 + \mathrm{A}\sqrt{16 + 9\mathrm{A}^2}}{2 - \mathrm{A}\sqrt{16 + 9\mathrm{A}^2}}$$

§ 251. If for one equivalent of sulphuric acid ($\frac{1}{2}H_2SO_4$) $n=2$, $(\mathrm{Av})_{\mathrm{A}} = 0{\cdot}49 = \frac{1}{x}$, and $x^2 = 4{\cdot}165$, it follows that $\mathfrak{p} = 0{\cdot}45$, $1 - \mathfrak{p} = 0{\cdot}55$.

If we bring together a dilute solution of one equivalent of soda with one equivalent of nitric acid and two equivalents or one molecular weight of sulphuric acid, the following changes take place:—

$$1NaOH + 1HNO_3 + 1H_2SO_4$$
$$= 0{\cdot}55\,NaNO_3 + 0{\cdot}45\,HNO_3 + 0{\cdot}45\,(\tfrac{1}{2}Na_2SO_4) + 1{\cdot}55\,(\tfrac{1}{2}H_2SO_4)$$
$$= 0{\cdot}55\,NaNO_3 + 0{\cdot}45\,HNO_3 + 0{\cdot}45\,NaHSO_4 + 0{\cdot}55\,H_2SO_4.$$

The avidity for equal molecular weights is

$$(\mathrm{Av})_{\mathrm{M}} = \frac{0{\cdot}45}{0{\cdot}55} = 0{\cdot}82,$$

and the coefficient x^2 used in calculating the molecular avidity is

$$\chi^2 = \left(\frac{1}{0{\cdot}82}\right)^2 = 1{\cdot}48.$$

If we let $x^2 = 4$, and $(\mathrm{Av})_{\mathrm{A}} = 0{\cdot}5$, we obtain $(\mathrm{Av})_{\mathrm{M}} = 0{\cdot}84$, and $\chi^2 = 1{\cdot}38$, which only differs slightly from the above results.

On the other hand, if the avidity for the molecular weight

is given, it is easy to calculate the avidity of the equivalent, *e.g.* for orthophosphoric acid Thomsen found

$$\mathfrak{M} = H_3PO_4,\ n = 3,\ (Av)_M = 0{\cdot}24.$$

i.e. if one equivalent of soda is mixed with one equivalent of nitric, and one molecular weight or three equivalents of orthophosphoric acid in dilute solution, the soda is distributed between the acids in the ratio of

$$1 : 0{\cdot}24 = \frac{1}{1{\cdot}24} : \frac{0{\cdot}24}{1{\cdot}24} = 0{\cdot}81 : 0{\cdot}19\,;$$

so that the solution contains

$$0{\cdot}81\,NaNO_3 + 0{\cdot}19\,HNO_3 + 0{\cdot}19\,NaH_2PO_4 + 0{\cdot}81\,H_3PO_4.$$

or, in equivalent weights,

$$0{\cdot}81\,NaNO_3 + 0{\cdot}19\,HNO_3 + 0{\cdot}19\,(\tfrac{1}{3}Na_3PO_4) + 2{\cdot}81\,(\tfrac{1}{3}H_3PO_4),$$

from which it follows that

$$x^2 = \frac{0{\cdot}81}{0{\cdot}19} \cdot \frac{2{\cdot}81}{0{\cdot}19} = 63{\cdot}0,$$

$$(Av)_A = \frac{1}{x} = 0{\cdot}13.$$

We also arrive at the same results if we start from the following considerations: If we mix the three bodies in their molecular proportions, viz. 3 equivalents of phosphoric acid to 1 equivalent of nitric acid and 1 of soda, the solution contains

$$p'\,(\tfrac{1}{3}Na_3PO_4) + p\,(\tfrac{1}{3}H_3PO_4) + q'\,NaNO_3 + q\,HNO_3.$$

The coefficients are determined by means of the equation

$$p + p' = 3,\quad q + q' = 1 = p' + q',\quad x^2 = \frac{p}{p'} \cdot \frac{q'}{q}\,;$$

so that we may also write

$$p'\,(\tfrac{1}{3}Na_3PO_4) + (3 - p')\,(\tfrac{1}{3}H_3PO_4) + (1 - p')\,NaNO_3 + p'\,HNO_3,$$

$$x^2 = \frac{3 - p'}{p'} \cdot \frac{1 - p'}{p'}.$$

But if we use molecular weights, and take into considera-

tion the fact that in reality only the acid phosphate is formed, we obtain for the same state of equilibrium the formula

$$p'\,(NaH_2PO_4) + (1-p')\,H_3PO_4 + (1-p')\,NaNO_3 + p'\,HNO_3,$$

so that $$\chi^2 = \frac{1-p'}{p'} \cdot \frac{1-p'}{p'},$$

and $$x^2 : \chi^2 = (3-p') : (1-p'),$$

$$\chi^2 = x^2 \frac{1-p'}{3-p'} = x^2 \cdot \frac{0{\cdot}81}{2{\cdot}81}.$$

Then the two avidities are

$$(Av)_A : (Av)_M = \chi : x = \sqrt{1-p'} : \sqrt{3-p'},$$

$$(Av)_A = \sqrt{\frac{1-p'}{3-p'}} \cdot (Av)_M = 0{\cdot}24 \sqrt{\frac{0{\cdot}81}{2{\cdot}81}} = 0{\cdot}13.$$

In the same way we obtain for an acid whose molecular weight is equal to n equivalents the general formula

$$(Av)_a : (Av)_M = \sqrt{1-p'} : \sqrt{n-p'},$$

in which p' may again be replaced by the value previously expressed by p.

§ 252. The avidities determined by Thomsen's[1] method are given in the following table. The values of $(Av)_A$ were, with the exception of phosphoric acid, determined by Thomsen; the values of $(Av)_M$, x^2, and χ^2 have been calculated by the author from Thomsen's results.

Acids	$\mathfrak{M}$	$(Av)_M$	χ^2	n	$(Av)_A$	x^2
Nitric	HNO_3	1	1	1	1	1
Hydrochloric	HCl	1	1	1	1	1
Hydrobromic[2]	HBr	0·89	1·26	1	0·89	1·26
Hydriodic[2]	HI	0·79	1·60	1	0·79	1·60
Sulphuric	H_2SO_4	0·83	1·48	2	0·49	4·16
Selenic	H_2SeO_4	0·75	1·78	2	0·45	5·00
Oxalic	$H_2C_2O_4$	0·40	6·25	2	0·26	14·8
Orthophosphoric	H_3PO_4	0·24	17·36	3	0·13	59·2
Citric	$H_3C_6H_5O_7$	0·09	123·5	3	0·05	400
Tartaric	$H_2C_4H_4O_6$	0·07	204	2	0·05	400
Hydrofluoric	HF	0·05	400	1	0·05	400
Acetic	$HC_2H_3O_2$	0·03	1100	1	0·03	1100
Boric	HBH_2O_3	0·01	10000	1	0·01	10000
Silicic	H_2SiO_3	0·00	—	2	0·00	—
Hydrocyanic	HCN	0·00	—	1	0·00	—

[1] *Pogg. Ann.* cxl. 505.

[2] According to W. Ostwald (*Journ. f. prakt. Chem.* [2] 1883, xxviii. 474) the avidity of HBr and HI is but little lower than that of HCl.

These numbers show that there is a great difference between the avidity of different acids, even when the acids exhibit a close similarity in their other properties. The difference between hydrochloric acid and the other three halogen acids is very striking. The high avidity of nitric acid as compared with that of ordinary phosphoric acid is less remarkable, in spite of the analogy between nitrogen and phosphorus compounds, as the former acid is monobasic, and the latter tribasic; but even metaphosphoric acid HPO_3, which is strictly analogous to nitric acid, appears to possess only a small avidity. As the acid is rapidly converted into orthophosphoric acid by the action of water, its avidity cannot be accurately determined. Oxalic acid has a much larger avidity than any other organic acid, even than citric acid.

From the following table, containing the avidity of the acids and the thermic effects[1] produced by neutralising one equivalent of the acid by soda, it is easy to see that this supposed measure of affinity would have arranged the acids in quite a different order.

Acids	Equivalent	$(Av)_A$	Thermic effect
Nitric	HNO_3	1	13680
Hydrochloric	HCl	1	13740
Hydrobromic	HBr	0·89	13750
Hydriodic	HI	0·79	13675
Sulphuric	$\frac{1}{2}H_2SO_4$	0·49	15690
Selenic	$\frac{1}{2}H_2SeO_4$	0·45	15195
Oxalic	$\frac{1}{2}H_2C_2O_4$	0·26	14140
Orthophosphoric	$\frac{1}{3}H_3PO_4$	0·13	11343[2]
Citric	$\frac{1}{3}H_3C_6H_5O_7$	0·05	12735
Tartaric	$\frac{1}{2}H_2C_4H_4O_6$	0·05	12655
Hydrofluoric	HFl	0·05	16270
Acetic	$HC_2H_3O_2$	0·03	13115
Boric	HBO_2H_2	0·01	10005
Silicic	$\frac{1}{2}H_2SiO_3$	0·00	2710
Hydrocyanic	HCN	0·00	2765

Hydrofluoric acid, which is one of the weakest acids, produces the greatest thermic effect. Sulphuric, selenic, and

[1] Thomsen, *Thermochemische Untersuchungen*, i. 294 and 308. The heat of neutralisation is also given in Gmelin-Kraut's *Handbuch*, i. p. 618; A. Naumann, *Thermochemie*, 356.

[2] *i.e.* $\frac{1}{3}$ of the thermic effect ($3NaOHAq, H_3PO_4Aq$). The first equivalent of soda gives 14829 °, *Pogg. Ann.* 1870, cxl. 91; *Thermochem. Untersuchungen*, i. 179.

oxalic acids also produce larger thermic effects than the four strongest monobasic acids. The heat of neutralisation of acetic acid is within 96% of that of nitric acid, although it is only capable of retaining 3 % of the base.

The avidity of boric acid has only been ascertained approximately. It is barely one per cent. of the avidity of nitric acid, but its thermic effect is 73 % of that of the latter acid. The avidity of silicic, stannic, chromic, hydrocyanic, and other weak acids is so small in comparison with that of nitric acid that it cannot be determined. Menschutkin [1] states that this also applies to the avidity of several bases, *e.g.* aniline and other substitution products of ammonia compared with the avidity of potash, or even, in certain cases, compared with that of trimethylamine or ammonia. Menschutkin concludes that the law of the action of mass does not apply in this case, but the author does not consider that this conclusion is justified.

The constant of affinity x may have any possible value between $x = 0, \frac{1}{x} = \infty$, and $x = \infty, \frac{1}{x} = 0$.

If it reaches one of these extremes, then the reaction will cease to be reversible.

The theory includes even the most extreme case.

It is very difficult to decide when such a case occurs. When $x > 1{,}000$, or even $x > 10{,}000$, our analytical methods are not, as a rule, sufficiently accurate for the purpose. The determination may, however, often be made by comparing the avidity of an acid or base with one possessing a feeble avidity instead of with the strongest.

H. Settegast [2] found the avidity of chromic acid as compared with acetic acid to be too small for measurement, but it is measurable when compared with carbonic acid.

§ 253. It is not only the thermic changes, but also other phenomena which accompany and vary with the chemical reactions that can be used for determining the influence of mass. Thomsen's experiments induced W. Ostwald [3] to in-

[1] *Ber. d. deut. chem. Ges.* 1883, xvi. 315.

[2] *Inaug. Dissertation*, Tübingen, 1878; *Wied. Ann.* 1879, vii. 242.

[3] In a series of articles, the first of which appeared in *Pogg. Ann.* 1876, Erg.-Bd. viii. 154. The remainder after 1877 appeared in the *Journ. f. prakt. Chem.*

vestigate for this purpose the changes which are produced in the density, and consequently in the volume of the solutions by the reaction. Although these changes are very small in dilute solutions, they are large enough to be measured with sufficient accuracy. In order to obtain comparable results, Ostwald always used solutions of such a strength that one kilogrm. of solution contained one equivalent weight in grams of the given substance. For example, one equivalent of potash, KOH = 56 g., is dissolved in 944 g. water, and the volume occupied by the 1,000 g. of the solution is found to be 950·669 cbc.[1] One equivalent, NH_3 = 17·0 g., dissolved in 983 g. of water, on the other hand, occupied a space of 1007·44 cbc., and one equivalent of HCl = 36·4 g., 982·406 cc. When an equivalent of this acid is mixed with an equivalent of each of the bases, instead of obtaining

982·406 + 950·668 = 1933·074 for KOH,
and 982·406 + 1007·440 = 1989·846 for NH_3,

the volumes were

1952·594 cc., or an increase of 19·52 cc. for KOH,
and 1983·274 cc., or a decrease of 6·572 cc. for NH_3.

In the first case an expansion, in the second a contraction has taken place, so that the change in volume shows whether potash or ammonia has neutralised the acid.

Solutions of polyvalent compounds were also prepared containing one equivalent in grams per kilogrm. The molecular weight of a dibasic acid was diluted with water to two kilograms, and that of a tribasic acid to three kilos. Ostwald adopted a similar method for salts.

The salt of a monobasic acid was prepared by mixing together one kilogram of the solution of the acid with one kilogram of that of the base, so that one equivalent weight of the salt is contained in two kilograms of the solution, and the neutral salt of a dibasic acid in four kilograms of solution, and so on.

With a view of determining the influence of mass Ostwald specially investigated the changes of volume which take place

[1] Ostwald took 1·0017 cc. of water, *i.e.* 1 gram of water at 20°, instead of 1 cbc., *i.e.* 1 gram of water at 4°, as the unit of volume, but this choice of unit does not, of course, influence the principle of the method.

when one acid is mixed with the salt of another acid. The following results were obtained.

Formula	Volumes before the reaction	Volumes after	Expansion
$K_2SO_4 + H_2N_2O_6$	3863·50 + 1933·20 = 5796·70	5810·70	+14·00
$K_2N_2O_6 + H_2SO_4$	3876·23 + 1936·81 = 5813·04	5810·67	− 2·37
$K_2SO_4 + H_2Cl_2$	3863·50 + 1964·81 = 5828·31	5841·39	+13·08
$K_2Cl_2 + H_2SO_4$	3907·06 + 1936·81 = 5843·87	5841·77	− 2·10

It is clear from these and many other observations of Ostwald's that the order in which the different substances are mixed has no influence on the nature of the solution obtained. The same volume is obtained whether nitric acid is added to the sulphate, or sulphuric acid to the nitrate. It is also obvious that the quantity of sulphate decomposed by nitric and hydrochloric acids is much larger than the quantity of nitrate or chloride decomposed by sulphuric acid, for in the former case the change of volume is + 14·0 or + 13, and in the latter only − 2·37 or −2·10. If these changes depended entirely on the given reaction they would serve directly as a measure of the reaction; the degree of decomposition would be proportional to the expansion. If the sulphate were decomposed by the nitric acid the expansion would be

$$5813{\cdot}04 - 5796{\cdot}70 = +16{\cdot}34.$$

But as the observed expansion is only + 14·0, the degree of decomposition would be

$$\frac{14{\cdot}00}{16{\cdot}34} = 0{\cdot}857, \text{ or } 85{\cdot}7\ \%.$$

The question is, however, not so simple, as secondary reactions take place which also exert an influence on the volume of the solution.

Let V be the volume which the solution would occupy if all the base was converted into nitrate, and V_2 the volume it would occupy if the base was converted into sulphate; then, in the previous case, $V_1 = 5813{\cdot}04$, and $V_2 = 5796{\cdot}70$.

Let v_1 be the expansion produced by the addition of nitric acid to the sulphate, and v_2 the (negative) expansion which really occurs on mixing the nitrate with sulphuric acid,

$$v_1 = + 14{\cdot}0,\ v_2 = - 2{\cdot}37.$$

If p equivalents of nitrate, and p equivalents of sulphuric acid are contained in the solution in both cases, we have

$$v_1 = p \cdot (V_1 - V_2) + \xi, \; v_2 = (1 - p)\,(V_2 - V_1) + \xi,$$

where ξ indicates the expansion due to secondary reactions, which is the same in both cases.

By subtracting one equation from the other we obtain

$$v_1 - v_2 = V_1 - V_2,$$

a result which closely agrees with experimental results, and is also obvious from theoretical considerations, for the expansion must be the same, whether the conversion into nitrate takes place at once or in two stages (first p, and then $1 - p$ equivalents). We therefore obtain $p = \frac{v_1 - \xi}{v_1 - v_2}$, from which the value of p can be calculated if that of ξ is known.

Special researches have shown that (just as in Thomsen's investigations, § 246) secondary reactions of considerable influence only occur between certain acids and their own salts, but not between both acids or both salts. These secondary reactions have been determined experimentally. They are relatively large in the case of sulphuric acid. For instance, Ostwald found:

Formulæ	Volumes before the reactions	Volumes after	Expansion ξ
$K_2SO_4 + \frac{1}{2}H_2SO_4$	3863·5 + 968·4 = 4831·9	4836·45	+ 4·55
$K_2SO_4 + H_2SO_4$	3863·5 + 1936·81 = 5800·31	5807·39	+ 7·09
$K_2SO_4 + 2H_2SO_4$	3863·5 + 3873·62 = 7737·12	7746·37	+ 9·25
$K_2SO_4 + 4H_2SO_4$	3863·5 + 7747·24 = 11610·74	11620·54	+ 9·80
$K_2SO_4 + 8H_2SO_4$	3863·5 + 15494·48 = 19357·98	19368·56	+ 10·58

The corresponding action of nitric acid was found to be too small for measurement. The value of p cannot be directly derived from the equation in the preceding paragraph, because ξ varies with p. By systematically trying different values for p, and replacing the corresponding values of ξ obtained by interpolation from the preceding table, Ostwald found that

$$p = 0{\cdot}667, \text{ and } 1 - p = 0{\cdot}333.$$

These investigations lead to exactly the same results as J. Thomsen obtained in his thermochemical research, viz.

when equivalent quantities of nitric and sulphuric acids act on one equivalent of potash, the nitric acid combines with twice as much of the base as the sulphuric acid does.[1]

§ 254. Ostwald has determined the *relative affinity* (identical with Thomsen's *avidity*) $\frac{p}{1-p} = \frac{1}{x}$, of a series of acids and bases at 20°, and also the effect of an increase in temperature on the sodium salts. His observations gave the following results:—

RELATIVE AFFINITY (AVIDITY).

Bases	$\frac{H_2N_2O_6}{H_2SO_4}$	$\frac{H_2Cl_2}{H_2SO_4}$	$\frac{H_2Cl_2}{H_2N_2O_6}$
Potash	$\frac{0.667}{0.333} = 2.00$	$\frac{0.659}{0.341} = 1.94$	$\frac{1.94}{2.00} = 0.97$
Soda	$\frac{0.667}{0.333} = 2.00$	$\frac{0.657}{0.343} = 1.92$	$\frac{1.92}{2.00} = 0.96$
Ammonia	$\frac{0.652}{0.348} = 1.88$	$\frac{0.644}{0.356} = 1.81$	$\frac{1.81}{1.88} = 0.96$
Magnesia	$\frac{0.638}{0.362} = 1.76$	$\frac{0.635}{0.365} = 1.74$	$\frac{1.74}{1.76} = 0.99$
Zinc oxide	$\frac{0.617}{0.383} = 1.61$	$\frac{0.605}{0.395} = 1.53$	$\frac{1.53}{1.61} = 0.95$
Copper oxide	$\frac{0.591}{0.409} = 1.44$	$\frac{0.584}{0.416} = 1.40$	$\frac{1.40}{1.44} = 0.97$
Soda 0°	$\frac{0.655}{0.345} = 1.90$	$\frac{0.659}{0.341} = 1.93$	$\frac{1.93}{1.90} = 1.02$
„ 20°	$\frac{0.667}{0.333} = 2.00$	$\frac{0.657}{0.343} = 1.92$	$\frac{1.92}{2.00} = 0.96$
„ 40°	$\frac{0.669}{0.331} = 2.02$	$\frac{0.666}{0.334} = 1.99$	$\frac{1.99}{2.02} = 0.98$
„ 60°	$\frac{0.703}{0.297} = 2.37$	$\frac{0.703}{0.297} = 2.37$	$\frac{2.37}{2.37} = 1.00$

The numbers in the fourth column are calculated from those in the second and third columns, because they cannot be directly determined with sufficient accuracy from the very small changes in volume.

The table shows that the avidity of nitric and of hydrochloric acids, as compared with that of sulphuric acid, increases with the strength of the base, and with the temperature. On the other hand, the relative avidity of hydrochloric

[1] *Vide* J. Thomsen's *Thermochem. Untersuch.* i. 148.

and nitric acids is constant. Ostwald deduces from these and from another series of experiments the rule that the avidity is constant. A few acids, more particularly sulphuric acid, on account of its peculiar nature, form exceptions to this law. Berthelot and Péan de Saint Gilles [1] have proved that the limit of etherification is constant within a wide range of temperature. Hence it appears that avidity, or Guldberg-Waage's constants of affinity, are independent of temperature.

The avidity of most acids has been proved to be independent of the nature of the base. Avidity, therefore, appears to be a characteristic constant for each acid.

§ 255. In the same way Ostwald has determined the avidity of other acids from the change in volume which results on mixing one of the acids with an equivalent quantity of the salt of another.

The following results were obtained for a series of monobasic acids :—

	Salt of	Free acid	Percentage of salt decomposed			
			Potash	Soda	Ammonia	Mean
1	Dichloracetic acid .	Nitric . .	77	77	75	76
2	,, ,, .	Hydrochloric .	74	75	73	74
3	,, ,, .	Trichloracetic .	72	71	71	71
4	,, ,, .	Lactic . .	8	9	11	9
5	Monochloracetic,, .	Trichloracetic .	92	92	92	92
6	Formic ,, .	,, .	97	96	97	97
7	,, ,, .	Lactic . .	43	46	48	46
8	,, ,, .	Acetic . .	25	23	23	24
9	,, ,, .	Butyric . .	21	21	19	20
10	,, ,, .	Isobutyric .	19	19	18	19
11	Butyric ,, .	Acetic . .	54	52	53	53
12	Isobutyric ,, .	,, . .	56	51	53	53
13	Propionic ,, .	Formic . .	78	80	79	79
14	Glycolic ,, .	,, . .	43	44	45	44

In order to compare the avidities of all the acids and refer them to the same unit of comparison, Ostwald calls the avidity of nitric acid 100, $Av(HNO_3) = 100$.

Then that of hydrochloric acid (from 1 and 2) is

$$Av(HCl) = 100 \cdot \frac{74}{76} = 98,$$

[1] *Ann. Chim. Phys.* [3] 1863, lxviii. 234. *Vide* § 243.

and for dichloracetic acid, direct from 1

$$\mathrm{Av}(HC_2HCl_2O_2) = 100 \cdot \frac{24}{76} = 32,$$

or, by comparison with hydrochloric acid, from 1 and 2,

$$\mathrm{Av}(HC_2HCl_2O_2) = 98 \cdot \frac{26}{74} + 34.$$

The mean is therefore 33.

For trichloracetic (3) and lactic acid (4) we have

$$\mathrm{Av}(HC_2Cl_3O_2) = 33 \cdot \frac{71}{20} = 80,$$

$$\mathrm{Av}(HC_3H_5O_3) = 33 \cdot \frac{9}{91} = 3{\cdot}3.$$

In the same way we can calculate the avidity of monochloracetic acid from trichloracetic, and that of formic acid and the other organic acids from lactic.

It is important to remember that the accuracy of the result is diminished when there is a great difference between the divisor and the number divided. For example, the avidity of formic acid, calculated from 3 and 6,

$$\mathrm{Av}(HCHO_2) = 80 \cdot \frac{3}{97} = 2{\cdot}5,$$

and from 4 and 7,

$$\mathrm{Av}(HCHO_2) = 3{\cdot}3 \cdot \frac{54}{46} = 3{\cdot}9.$$

The latter result is the more accurate.

In this way Ostwald calculated the following table of avidities, which he does not regard as perfectly accurate, but sufficiently so to give the acids in their correct order.

Acids		Avidity	Acids		Avidity
Nitric . .	HNO_3	100	Lactic . .	$HC_3H_5O_3$	3·3
Hydrochloric .	HCl	98	Malic . .	$\frac{1}{2}H_2C_4H_4O_5$	2·82
Trichloracetic .	$HC_2Cl_3O_2$	80	Succinic .	$\frac{1}{2}H_2C_4H_4O_4$	1·45
Dichloracetic .	$HC_2HCl_2O_2$	33	Acetic . .	$HC_2H_3O_2$	1·23
Monochloracetic	$HC_2H_2ClO_2$	7·0	Propionic .	$HC_3H_5O_2$	1·04
Tartaric . .	$\frac{1}{2}H_2C_4H_4O_6$	5·2	Butyric . .	$HC_4H_7O_2$	0·98
Glycolic . .	$HC_2H_3O_3$	5·0	Isobutyric .	$HC_4H_7O_2$	0·92
Formic . .	$HCHO_2$	3·9			

§ 256. These numbers show in a very instructive manner the influence which the nature, number, and arrangement of the atoms exert on the avidity of the acids.

Acid		Avidity	Acid		Avidity
Formic	HOCHO	2·9	Propionic	$HOCOCH_2CH_3$	1·04
Difference	CH_2	2·67	Difference	O	2·3
Acetic	$HOCOCH_3$	1·23	Lactic	$HOCOCH_2OHCH_3$	3·4
Difference	CH_2	0·13			
Propionic	$HO.COC_2H_5$	1·06	Acetic	$HOCOCH_3$	1·2
Difference	CH_2	0·06	Difference	$-H+Cl$	5·8
Butyric	$HOCOC_3H_7$	0·98	Monochloracetic	$HOCOCH_2Cl$	7·0
			Difference	$-H+Cl$	26
Acetic	$HOCOCH_3$	1·23	Dichloracetic	$HOCOCHCl_2$	33
Difference	O	3·9	Difference	$-H+Cl$	47
Glycolic	$HOCOCH_2OH$	5·0	Trichloracetic	$HOCOCCl_3$	80

The avidity is diminished by additional carbon atoms combined with hydrogen. It is considerably increased by an addition of oxygen, by the substitution of OH for H, but a much larger increase occurs when hydrogen is replaced by chlorine. It is very remarkable that the first chlorine atom increases the avidity of acetic acid by 5·8, the second by 26, and the third by 47. This must be due to the hydrogen exerting an opposite action to the chlorine. The two atoms of H neutralise to a great extent the action of the one atom of chlorine in monochloracetic acid. The one atom of hydrogen in the presence of two chlorine atoms in the dichloracetic acid exerts a much smaller action, and in the trichlorinated acid this neutralising action ceases. At the present time the law of these opposing influences cannot be formulated.

The protest which Berzelius raised in the well-known discussion with Dumas and his school against the doctrine that the chlorine in trichloracetic acid 'plays the same part' as the hydrogen in acetic acid, is to a certain extent justified by the existence of this fact. Now that the extreme views formerly held by each of the two opposing parties have given place to more impartial opinions, no one will deny that the same electronegative nature of chlorine which causes hydrochloric acid to be an acid also causes trichloracetic acid to be so much more powerful an acid than the analogously constituted

acetic acid. It also confirms the soundness of the view that it is the position of the atoms which determines their influence on the properties of the compound; for even the three chlorine atoms in trichloracetic acid cannot produce an acid which is so strong as hydrochloric acid, obviously because in the latter case the chlorine is directly combined with the hydrogen, but in the former it is only indirectly combined.

§ 257. In addition to the changes in volume which accompany the neutralisation of different acids, Ostwald [1] made use of the changes in refractive power, in order to investigate the distribution of a base between two acids. The investigation was conducted in a similar manner to that of the preceding research. It yielded the following results:—

Salt of	Free acid	Percentage of salt decomposed			
		K_2O	Na_2O	NH_3	Mean
Dichloracetic acid .	Nitric . . .	80	81	78	80
„ „ .	Hydrochloric . .	80	73	71	75
Lactic „ .	Dichloracetic . .	88	91	90	90
„ „ .	Formic . . .	59	63	55	59
Trichloracetic „ .	Monochloracetic .	10	9	11	10
Propionic „ .	Formic . . .	80	79	74	78
Butyric „ .	„ . . .	73	75	79	76
Isobutyric „ .	„ . . .	74	74	73	74
Formic „ .	Isobutyric . .	26	26	25	26
Acetic „ .	Butyric . . .	38	50	30	39
„ „ .	Isobutyric . .	31	45	44	40

These results agree with the preceding results quite as closely as could be expected when two totally different experimental methods are employed.

	Volumetric	Optical
Dichloracetic acid : Nitric acid . . .	=24 : 76	20 : 80
„ „ : Hydrochloric acid .	=26 : 74	25 : 75
„ „ : Lactic acid . .	=91 : 9	90 : 10
Trichloracetic acid : Monochloracetic acid .	=92 : 8	90 : 10, &c.

The volumetric results must be regarded as the more exact. Their accuracy is confirmed [2] by those deduced from the optical

[1] Dissertation on *Volumchemische und optischchemische Studien*, Dorpat, 1878, 35; *Journ. f. prakt. Chem.* 1878, xviii. 328.

[2] Ostwald, *Dr. Diss.* 27; *Journ. f. prakt. Chem.* xviii. 352.

method. The coefficients of affinity of coloured acids and salts may also be determined by quantitative spectrum analysis.[1]

§ 258. The values of the avidities determined by either of these methods give rise to some remarkable comparisons.[2] As a rule, the larger the avidity of an acid, the larger will be the expansion which accompanies the neutralisation of the acid, although one would be inclined to assume that the stronger acid would attract the base more closely, and therefore cause a contraction. In the following table the expansion on neutralising acids by potash and ammonia is expressed according to the standard given in § 253.

Acid	Avidity	Expansion on neutralisation with		Difference
		KOH	NH_3	
Nitric	100	+20·05	− 6·44	26·49
Hydrochloric . .	98	19·52	− 6·57	26·09
Trichloracetic . .	80	17·36	− 8·67	25·93
Dichloracetic . .	33	12·95	−12·98	25·93
Monochloracetic . .	7·0	10·85	−15·09	25·94
Glycolic . . .	5·0	9·62	−16·50	26·12
Formic	3·9	(12·36)	−(13·60)	25·96
Lactic	3·3	8·27	−17·74	26·01
Acetic	1·23	(9·52)	−(16·26)	25·78
Propionic . . .	1·04	7·83	−17·82	25·65
Butyric	0·98	7·01	−18·63	25·64
Isobutyric . . .	0·92	6·30	−19·27	25·57

With increasing avidity the expansion on neutralisation with potash increases, and the contraction (negative expansion) with ammonia decreases.

The stronger the acid, the larger the expansion, or the smaller the contraction will be. In the middle of the table formic and acetic acids are exceptions to the rule if they are compared with their immediate neighbours, but are not exceptions when compared with more distant acids in the table.

The expansion which the solutions of strong acids and bases experience on neutralisation is supposed by Müller Erzbach[3] to be due to the fact that the free bases and acids give a greater contraction with water than their salts do.

[1] H. Settegast, *Inaug. Diss.* Tübingen, 1878; *Wied. Ann.* 1879, 242.

[2] Ostwald, *Journ. f. prakt. Chem.* [2] xviii. 363; *Dr. Diss.* 38.

[3] *Programm Nr.* 606 *der Hauptschule zu Bremen*, 1879, 26; *Liebig's Annalen*, 1883, ccxxi. 127.

Both Ostwald's and Thomsen's researches (§ 252) show that the heat of neutralisation frequently sinks when the avidity increases, and *vice versâ*. For example, the avidity of the organic acids $C_nH_{2n}O_2$ diminishes with an increase in the molecular weight, but their heat of neutralisation increases (§ 224).

§ 259. Laws similar to those which hold good for dilute solutions govern the influence of mass in gases; but, although it was in this field of research that the new investigation of the action of mass was commenced by Bunsen's work (§ 240) 'On the Relative Affinity of different Gases for Oxygen,' which was afterwards followed by a series of investigations, the laws of the action of mass for gases have not been ascertained with the same degree of accuracy as the laws dealing with substances in solution. This may probably be explained by the fact that only one form (which is by no means the simplest) of the problem has been investigated. E. v. Meyer,[1] A. Horstmann,[2] and K. Bötsch,[3] following in Bunsen's [4] footsteps, have investigated the distribution of oxygen (in insufficient quantity for complete combustion) between two different combustible gases. The mixture was ignited by an electric spark, and the products of combustion estimated. The influence of mass is very obvious: an increase of one of the combustible gases is always accompanied by an increase in its products of combustion. But the law affecting this increase is not clearly known. Horstmann found that with a constant percentage of oxygen in the mixture, and varying amounts of the two combustible gases, that the ratio between products of combustion is proportional to the ratio of the unburnt substances. In this case the law of Guldberg and Waage would hold good, and the mixture formed by the incomplete combustion of carbon monoxide and hydrogen,

$$pH_2 + qCO + p'H_2O + q'CO_2,$$

[1] *Journ. f. prakt. Chem.* [2] x. 273; xiii. 125; xviii. 290.

[2] *Lieb. Ann.* 1878, cxc. 228; *Ber. d. deut. chem. Ges.* 1877, x. 1626; 1879, xii. 64.

[3] *Inaug. Diss.* Tübingen, 1881; *Lieb. Ann.* ccx. 207.

[4] *Lieb. Ann.* 1853, lxxxv. 137; *Gasom. Methode*, 2. Aufl. 340.

is determined by the equation

$$x^2 = \frac{p}{p'} = \frac{q}{q'},$$

$$p + p' = \mathrm{P},\ q + q' = \mathrm{Q},\ p' + q' = 2\mathrm{O},$$

when P, Q, and O indicate the volumes of hydrogen, carbon monoxide, and oxygen. The coefficient x^2 cannot correctly be called a constant, as it not only varies with the ratio of O : (P + Q), but also with the temperature at which the mixture is ignited, with the pressure, and even with the dimensions of the eudiometer employed. Nevertheless, the law of Guldberg and Waage may hold good for all cases which are strictly analogous to those discussed in the preceding paragraphs.

The simultaneous combustion of two gases, *e.g.* hydrogen and carbon monoxide, with free oxygen, is a less simple process than the decomposition of the salt of one acid by another acid ; for in the latter case only two reactions hold each other in equilibrium, but in the former four different reactions are possible, viz. the oxidation of each of the two gases by oxygen, and the reduction of each of the products of combustion by the excess of the other combustible gas :

$2H^2 + O_2 = 2H_2O$	$H_2 + CO_2 = H_2O + CO$
$2CO + O_2 = 2CO_2$	$CO + H_2O = CO_2 + H_2$

Only the two last reactions are strictly analogous to those we have been considering, and it has not even been ascertained with certainty whether they do take place to any considerable extent in the short moments of ignition. The possibility of such a reaction has no doubt been proved experimentally. The law of Guldberg and Waage could in all probability be more easily confirmed by exposing the mixture of H_2 and CO_2 or H_2O and CO for a longer time, at a sufficiently high temperature. Under these conditions the results may be quite different from those obtained by exploding and at once cooling the mixture. For example, Bötsch [1] has shown that when hydrogen is exploded with a mixture of chlorine and oxygen, it only combines with the former ; but, on the other hand,

[1] § 230.

when oxygen and hydrochloric acid are passed through red-hot tubes, the oxygen takes away a portion of the hydrogen from the chlorine.

§ 260. Berthollet has pointed out that the action of mass is materially influenced by the state of aggregation of the bodies taking part in the reaction, and of the products of the double decomposition. But as he directed his attention more especially to the changes which take place in solutions, he was of opinion that when one or more of the combinations produced by the mutual action of the substances in solution, is insoluble or sparingly soluble, and separates out in the solid or gaseous state, these insoluble compounds will be the chief, in many cases the sole products.

Berthollet explained these facts by assuming that, in the first case, all the possible combinations are produced, the insoluble compounds are precipitated, the gaseous compounds escape. The state of equilibrium is disturbed, and consequently new quantities of the insoluble products continue to be formed so long as there is sufficient material present for their formation. This hypothesis corresponds in its main features with the results of observation, but it is erroneous in regarding a substance deposited from a solution in the solid form as perfectly devoid of action. We know that a precipitate may act to a greater or less degree on the substances which remain in solution, and consequently it does not cease to influence the condition of the liquid mixture.

The chemists who followed Berthollet in the investigation of this subject, more especially Debus and Chižinski, devoted their attention to the influence which a precipitate exerts on the composition of the liquid in which it is formed. Debus investigated the precipitation of lime and baryta by a small quantity of carbonic acid, which was far from sufficient for their complete precipitation. Chižinski also investigated the precipitation of calcium and magnesium chlorides by small quantities of ammonium phosphate.

They proved beyond doubt that the amount of one or other of the two bases in the precipitate increases and diminishes with the relative amount of that substance in the solution, and that each of the bases investigated can by its mass gra-

dually displace the other from the precipitate. They could not find a simple law for the relation existing between the composition of the precipitate and that of the solution.

Guldberg and Waage were the first to accomplish this object. They reversed the problem and investigated the action of a precipitate formed in, or brought into a solution on the dissolved salts. They found that the state of equilibrium is chiefly determined by the condition of the substances remaining in solution and that the quantity and composition of the precipitate (within very wide limits) exerts no influence if neither of the undissolved compounds is present in very minute quantities.[1] If the necessary minimum is present, the quantity may be considerably increased without affecting the state of equilibrium. Guldberg and Waage therefore used the equation in § 242, $x^2 \frac{p}{p'} = \frac{q}{q'}$, in which the coefficients of the insoluble compounds are assumed to be constant.

§ 261. The simplest case for consideration is when two of the substances are insoluble, *e.g.* two salts of one of the acids or bases in question. In this case p' and q' are constant, but not equal, and $p = q$. *const.*

Each of the soluble substances acts continuously on one of the two insoluble compounds, and equilibrium is produced when the decompositions effected by the former, and that produced by the latter, in the same space of time are equal.

Both decompositions are independent of the quantity of the insoluble compound; they must, therefore, be proportional to the quantity of substance in solution. If the carbonates and sulphates of potassium and barium are the four compounds, then the quantities p . K_2SO_4 and $q K_2CO_3$ remaining in solution are determined by the equation γ . $p = q$, assuming, of course, that sufficient $BaSO_4$ and $BaCO_3$ remain in contact with the solution to permit of this state of equilibrium being established. A very long time is frequently required to bring about the state of equilibrium.

Experiments with boiling-hot tolerably dilute solutions gave the following results: $\gamma = 4$, $q = 4p$.

This equation means, then, that the insoluble $BaCO_3$ is

[1] *Journ. f. prakt. Chem.* [2] xix. 89.

decomposed by K_2SO_4 four times as rapidly as the sulphate $BaSO_4$ is decomposed by K_2CO_3. Experiments especially directed to the influence of time on these decompositions confirmed the conclusion that the former decomposition takes place much more rapidly than the latter. The coefficient γ is not invariable ; on the contrary, its value changes with the temperature, with the quantity of the solvent, and occasionally with the condition of the precipitate, whether it is crystalline or amorphous, whether it was precipitated hot or cold, whether it has been previously dried, or whether it has been kept moist, &c. This is perfectly obvious, since all these external conditions influence the action of the bodies in solution on the insoluble compounds. Their influence, as a rule, varies with the nature of the substances.

In the example given, γ increases considerably with the quantity of the solvent, and decreases with a rising temperature. We can therefore conclude that the reaction

$$K_2SO_4 + BaCO_3 = BaSO_4 + K_2CO_3$$

is less delayed by diluting the solution and less facilitated by increasing the temperature than the reverse reaction,

$$K_2CO_3 + BaSO_4 = K_2SO_4 + BaCO_3.$$

The dilute solution contains more carbonate in proportion to sulphate than the concentrated solution, and the cold more than the hot solution does.

§ 262. The exact determination of the coefficient γ is difficult, especially when the state of equilibrium is very slowly attained. Guldberg and Waage [1] left the mixtures

$$\text{I. } 1BaSO_4 + 1K_2CO_3 + 100H_2O,$$
$$\text{II. } 1BaCO_3 + 1K_2SO_4 + 100H_2O,$$

at a temperature of 3° for more than a year, and then found the solutions contained

I.	II.
0·959 K_2CO_3	0·929 K_2CO_3
0·041 K_2SO_4	0·071 K_2SO_4
$\gamma = 23·4$	$\gamma = 13·1$

[1] *Études*, &c., p. 18.

Equilibrium had evidently not been established. The correct value of γ lies between these values, as it has been shown that the final state of equilibrium is independent of the original form in which the bodies are combined. Increasing the quantity of the insoluble body, and raising the temperature, hastens the establishment of the state of equilibrium; diminishing the solvent generally has the same effect, but occasionally the reverse.[1]

Guldberg and Waage obtained the following results at the temperature of the boiling-point of the mixtures in t hours:—

$1BaSO_4+1K_2CO_3+nH_2O$					$1BaCO_3+1K_2SO_4+nH_2O$				
K_2SO_4	K_2CO_3				K_2SO_4	K_2CO_3			
p	q	n	t	γ	p	q	n	t	γ
0·27	0·73	66·67	36	2·6	—	—	—	—	—
0·24	0·76	100	70	3·2	0·28	0·72	100	72	2·6
0·18	0·82	500	70	4·6	0·20	0·80	500	403	4
0·16	0·84	1000	79	5·3	(0·30)	(0·70)	1000	45	2·3

The state of equilibrium was far from being attained in the last experiments; in the others it had been approximately reached. This shows that γ, *i.e.* the quantity of carbonate, increases with the quantity of water without reaching the limits found at the lower temperature $23 > \gamma > 13$.

The authors obtained similar numbers when they substituted sodium for potassium salts. James Morris [2] has investigated the mutual action between the carbonates and chromates, and the carbonates and sulphates of potassium and barium by a somewhat different method. He ascertained the composition of the precipitates which were produced by barium chloride in a mixture of these potassium salts. He found the ratio of the carbonate (q) to the chromate (p) remaining in the solution, at the ordinary temperature, to be

$$\gamma = \frac{q}{p} = 10, \text{ in round numbers.}$$

If the precipitate is left in the solution the quantity of carbonate in the solution is increased as a portion of the un-

[1] The precipitation of barium as chromate takes place more rapidly in dilute solutions (Ostwald, *Journ. f. prakt. Chem.* [2] 1880, xxii. 259).

[2] *Inaug. Diss.* Tübingen, 1879; *Annalen*, 1882, ccxiii. 253.

decomposed K_2CrO_4 is gradually changed into $BaCrO_4$. At 100° the precipitate contains much more carbonate; the mean value of γ was found to be 3·75, but the results of different experiments varied considerably. In the case of carbonate and sulphate Morris found that γ was very slightly influenced by the temperature. The mean of the results for cold solutions is $\gamma = 3{\cdot}5$, and $\gamma = 3{\cdot}2$ for boiling solutions.

The values are but slightly affected by a moderate change in the quantity of the solvent. The errors of experiment may affect these results to a considerable extent, as the composition of the liquid is calculated from the analysis of the precipitate. These values for γ must be regarded as only approximate.

In a research on the mutual action between the carbonates and oxalates of the alkaline earths and those of sodium, W. Smith[1] found that for each of the metals Ca, Sr, Ba, the power of combining with oxalic acid diminishes, and that of uniting with carbonic acid increases, with the value of the atomic weight of the metal. This is true at all temperatures. Lead, like barium, unites with more carbonic than oxalic acid.

Na_2CO_3 formed from $Na_2C_2O_4$			$Na_2C_2O_4$ formed from Na_2CO_3		
By the carbonates	cold	hot	By the oxalates	cold	hot
$CaCO_3$	19·8 %	22·9 %	CaC_2O_4	16·1 %	52·3 %
$SrCO_3$	7·6	7·6	SrC_2O_4	57·2	80·0
$BaCO_3$	4·8	5·0	BaC_2O_4	73·2	88·0
$PbCO_3$	6·4	13·1	PbC_2O_4	81·5	90·6

Although the final state of equilibrium does not appear to have been reached in these experiments, they nevertheless show the preference of calcium for oxalic acid, and of barium for carbonic acid.

§ 263. The theoretical consideration of the case in which only one of the bodies is insoluble is rather more complicated. We have an example of this kind when a base is brought in contact with two acids and forms an insoluble salt with one of them, or when an insoluble salt is added to an acid which forms a soluble salt with the base, but precipitates the acid.

This case has been investigated by Ostwald,[2] and, at the

[1] *Chem. Soc. Journ.* 1877, ii. 245.

[2] *Journ. f. prak. Chem.* [2] 1877, xvi. 421; 1879, xix. 468; 1880, xxii. 251; 1881, xxiv. 486.

instigation of Guldberg and Waage, by S. Wleugel,[1] and also by Horstmann.[2] Guldberg and Waage[3] applied their theory to this special case by simply regarding the coefficients (q') of the insoluble substances as constant. In this way they obtained the equation $x^2q' = \frac{p' \cdot q}{p} = c$. Its correctness was tested by a series of experiments on the precipitation of solutions of calcium chloride by oxalic acid, and the decomposition of calcium oxalate by hydrochloric acid.

Q equivalents of oxalic acid ($H_2C_2O_4$) were added to 111 centigrammes of $CaCl_2$ (*i.e.* the molecular weight expressed in centigrammes); the mixture was diluted to 1·1 litres, and after three days the quantity of calcium oxalate which had been precipitated was estimated. Let ξ represent the equivalents of calcium oxalate precipitated, then it will also express the equivalent quantity of hydrochloric acid which has been liberated, and we have in solution

$$\xi H_2Cl_2 + (Q - \xi) H_2C_2O_4 + (1 - \xi) CaCl_2,$$

$$p = \xi, \quad q = Q - \xi, \quad p' = (1 - \xi),$$

$$c = \frac{(Q - \xi)(1 - \xi)}{\xi};$$

hence $$\xi = \tfrac{1}{2}[1 + Q + c \pm \sqrt{(1 + Q + c)^2 - 4Q}]$$

From this formula it follows that $c = 0{\cdot}0215$ the value of ξ, a result which agrees with experiment. Ostwald[4] has, however, recently pointed out that this formula is not well adapted to test the accuracy of the theory, because the very small value c can only exert a slight influence on the results of the calculation.

Let $c = 0$, then $\xi = \frac{1}{2}[1 + Q \pm (1 - Q)]$.

The roots of this equation are $\xi = 1$ and $\xi = Q$, and $p' = 0$ or $q = 0$; *i.e.* either all the calcium chloride or all the oxalic acid will be precipitated. In reality this represents very nearly what happens. The small quantity remaining in solution cannot be correctly calculated by the formula. If we attempt to deduce the value of the constant c from these observations, we obtain values which vary between 0·0176 and

[1] *Journ. f. prak. Chem.* 1879, xix. 93–95.

[2] *Nat. Med. Verein zu Heidelberg*, N.S. ii. 247.

[3] *Journ. f. prak. Chem.* [2] 1877, xvi. 421; 1879, xix. 468; 1880, xxii. 251; 1881, xxiv. 486.

[4] *Ibid.* 1881, xxiv, 486.

0·0386. The number Guldberg and Waage used for c is 0·0215, which was deduced from an observation made by Ostwald.

§ 264. On closer consideration doubts arise as to the equation $\frac{p'q}{p} = c$, $p'q = cp$, which is at the foundation of the theory. It is derived from the chief equation (§ 242) $kpq' = k'p'q$, or $xpq' = \frac{1}{x}\, p'q$, in which q', and consequently $k \,.\, q'$, are assumed to be constant. This simplification is not permissible. The right side of the equation states that the quantity of calcium oxalate formed in the unit of time is proportional to the amount of calcium chloride (p') and oxalic acid (q) in solution, but the left side of the equation asserts, when we assume $k \,.\, q' = \text{const.}$, that the decomposition of the oxalate by the hydrochloric acid is proportional to the amount of hydrochloric acid (p) in the solution. Although this relation has been proved for two bodies in solution by the observations described in §§ 241–255, according to Guldberg and Waage [1] it does not exist when a body in solution acts on an undissolved substance; on the contrary, the action increases more rapidly than the concentration for some bodies, and less rapidly for others. Consequently the hypothesis propounded by Guldberg and Waage for this case is improbable, and is not confirmed by experience.

§ 265. Ostwald left calcium oxalate in contact with hydrochloric acid of different degrees of concentration (n litres containing a double equivalent $H_2Cl_2 = 72{\cdot}74$ grammes). The following table shows the quantities which had passed into solution, expressed in double equivalents, in grammes per 100 litres, or milligrammes per 100 cc.

Temp.	$\frac{H_2Cl_2}{p}$	$\frac{CaCl_2}{p'}$	$\frac{H_2C_2O_4}{q}$	$c = \frac{p'q}{p}$	n
20°	23292	1·708	1·708	0·125	4
"	4612	0·388	0·388	0·033	20
Ordinary temp.	2220	0·280	0·280	0·035	40 [2]
100°	19012	5·988	5·988	1·887	4
"	3692	1·308	1·308	0·464	20
"	0702	0·409	0·409	0·238	90

[1] *Études sur les Affinités*, 65, 74.

[2] The whole of these numbers uncertain, in consequence of a misprint in the original, making it doubtful whether H_2Cl_2 is dissolved in 30 or 40 litres.

The value of c is by no means constant, but increases considerably with the number of equivalents of hydrochloric acid contained in the solution. Hence we conclude that the action of the acid on the oxalate increases with the concentration, but more rapidly than the latter. A rise in temperature increases the action of the hydrochloric acid to a much greater extent than it affects the mutual action of the other bodies in solution. The quantity of the latter consequently decreases.

In the chief equation $kpq' = k'p'q$, let $p \,.\, q'$ be replaced by the sign of an unknown function of p instead of by the constant c, then the condition of equilibrium will be $x^2 \,.\, f(p) = p' \,.\, q$. This is symmetrical for p' and q, and expresses the fact that the condition of the solution depends in precisely the same way on the quantity of calcium chloride (p') as it does on the amount of oxalic acid (q). Ostwald's experiments show that this is actually the case. He mixed the hydrochloric acid with an excess (E) of calcium chloride or oxalic acid before bringing it in contact with the oxalate. In the first case the state of equilibrium is

$$p\mathrm{H_2Cl_2} + (1 - p)\,\mathrm{H_2C_2O_4} + (\mathrm{E} + 1 - p)\,\mathrm{CaCl_2},$$

in the second

$$p\mathrm{H_2Cl_2} + (1 - p)\,\mathrm{CaCl_2} + (\mathrm{E} + 1 - p)\,\mathrm{H_2C_2O_4},$$

but in both $x^2 f(p) = p' \,.\, q = (1 - p)(\mathrm{E} + 1 - p)$.

The following table gives the values of p, $1 - p$, and c, which were observed when the excess of $\mathrm{CaCl_2}$ or $\mathrm{H_2C_2O_4}$ (mentioned under E in the first column) was used. Temperature, 20° C.; dilution, $\mathrm{H_2Cl_2}$ in four litres.

E	p		$p'-1-p=q$		c	
	$CaCl_2$	$H_2C_2O_4$	$CaCl_2$	$H_2C_2O_4$	$CaCl_2$	$H_2C_2O_4$
0	0·9317		0·0683		0·0050	
0·05	0·9499	0·9501	0·0501	0·0499	0·0053	0·0053
0·10	0·9601	0·9613	0·0390	0·0387	0·0056	0·0056
0·15	0·9691	—	0·0309	—	0·0058	—
0·20	0·9739	0·9738	0·0261	0·0262	0·0061	0·0061
0·30	0·9805	0·9805	0·0195	0·0195	0·0064	0·0064
0·40	0·9845	—	0·0155	—	0·0066	—
0·50	0·9868	0·9868	0·0132	0·0132	0·0068	0·0068
0·70	0·9895	—	0·0105	—	0·0075	—
1·00	0·9915	0·9917	0·0085	0·0083	0·0087	0·0085

Ostwald points out that not only these results, but also those obtained at 100° with solutions five times more dilute, and the results obtained when nitric acid is used instead of hydrochloric acid, all indicate (1) that the supposed constant $c = \frac{p'q}{p} = \frac{(1-p)\,(E+1-p)}{p}$ is a variable quantity,[1] and (2) that the function $x^2f(p) = p \,.\, c$ is symmetrical with regard to p' and q. Without further experiments, all we can at present add regarding the character of this function is that it increases rapidly with an increase in temperature, and it increases much more rapidly than p for an increase in E. For example (temperature, 100°; dilution, H_2Cl_2 in 4 litres) :—

E	p		$1-p$		c	
	$CaCl_2$	$H_2C_2O_4$	$CaCl_2$	$H_2C_2O_4$	$CaCl_2$	$H_2C_2O_4$
0	0·7605		0·2395		0·075	
0·2	0·8143	0·8159	0·1857	0·1841	0·088	0·087
0·5	0·8637	0·8648	0·1363	0·1352	0·100	0·101
1·0	0·9046	0·9077	0·0954	0·0923	0·115	0·111

Hence we have the following values for $c \,.\, p = x^2f(p)$:—

Temp.	E = 0	0·2	0·5	1
20°	$x^2f(p) = 0·0047$	0·0059	0·0068	0·0086
100°	,, = 0·0574	0·0716	0·0867	0·1045

Further experimental investigations are required to discover the law which governs these results.

§ 266. If under the conditions of the experiment, one of the substances is gaseous, but more or less soluble in the liquid, then its action is weakened in proportion to the amount which escapes from the solution, for it is only the quantity remaining in the solution which operates as an 'active mass.' In other

[1] In calculating c, different values can be obtained from one and the same observation, according to the magnitude of the volume of solution taken into account. For example, if the first observation in the table is calculated for 1 instead of 4 litres of liquid, then we find

$$p = 0·2329,\ q = p' = 0·01771,\ c = 0·00125, \text{ instead of } 0·005,$$

which clearly shows that the value c is not a suitable form of expression for the relative affinities.

respects, the same laws which are valid for substances in solution apply in this case.

The volatility of many acids is the cause of their expulsion from their salts by acids of lower avidity. For example, at a high temperature sulphuric acid expels nitric and hydrochloric acids, but all three are expelled by silicic and phosphoric acids at a red heat.

When the simultaneous formation of insoluble and volatile bodies is possible then the nature of the bodies taking part in the reaction and external conditions determine what compounds will be produced. A small change in the conditions of the experiment often reverses a reaction. Acetic acid decomposes aqueous solutions of alkaline carbonates with evolution of carbonic acid, but a solution of an acetate in absolute alcohol is decomposed by carbonic acid, the carbonate is precipitated, and acetic acid and ethyl acetate are formed.

§ 267. The fact that the action of mass is one of the most important factors in chemical mechanics is more and more recognised as the science advances. Half a generation ago Guldberg and Waage[1] wrote with truth: 'Investigations of this subject are without doubt more difficult, more tedious, and less productive of results than the researches which at present occupy the majority of chemists, *i.e.* the discovery of new compounds. According to our views, nothing can more rapidly elevate chemistry to the rank of a truly exact science, than just these investigations with which our research has dealt.'

The widely spread opinion that the measurement of the affinities can be accomplished by merely determining the thermic effects, is to a great extent the reason why only a few valuable researches have been conducted in this field of investigation. But even now the opinion begins to gain ground that the importance of thermic effects for ascertaining the nature of chemical changes has been over-estimated.

The connection between the thermic effects, the changes of density, specific heat, refractive power and numerous other phenomena attendant on chemical reactions, and the inner cause of these changes, *i.e.* the *affinity*, can only be ascertained

[1] *Études*, p. 74.

by impartially investigating the changes which actually take place. We must assign the stronger affinity to that body which under similar conditions, displaces the others from their compounds, not to the one which is displaced. The notion that affinity is intimately associated with this or the other phenomenon cannot relieve us of the duty of directly determining these co-efficients of affinity by experiment. Any indirect conclusion is untrustworthy, and may be the cause of serious errors.

The expansion of Guldberg and Waage's theory will be one of the first problems for investigation with especial reference to the non-reversible reactions. It is true that they are recognised by this theory as they represent the case in which $x=0$ and $\frac{1}{x}=\infty$ (§ 252).

But the disappearance of one of the co-efficients of affinity nullifies the assumption which the theory makes, that a state of equilibrium results from two contending and antagonistic reactions, so that it is doubtful whether it is the same theory or a similar theory which is applicable to this case. It is all the more remarkable that numerous observations have proved that the course of non-reversible reactions is really similar to that of reversible reactions.

If the formation of anilides,[1] nitro-derivatives,[2] sulphonic acids, the so-called contact actions,[3] the decomposition of unstable compounds[4] and other non-reversible reactions follow the same laws which govern the formation of salts, ethers, and other reversible reactions, this is probably due, to a great extent, to the fact that the time which is required for the establishment of equilibrium is, in each class of reaction, dependent in the same manner on the acting mass. The non-reversible processes appear to be the more simple as we have only to study the dependence of one instead of two de-

[1] *Ber. d. deut. chem. Ges.* 1882, xv. 1977.

[2] P. Spindler, Inaug. Diss. Tübingen, 1883; *Ber. d. deut. chem. Ges.* 1883, xvi. 1252.

[3] W. Ostwald, 'Studien zur chemischen Dynamik,' *Journ. f. prakt. Chem.* [2] 1883, xxvii. 1; xxviii. 449.

[4] M. Landolt, 'Die Existenzdauer der unterschwefeligen Säure in wässerigen Lösungen,' *Sitz.-Ber. Akad. Wiss.* Berlin, 1883, 1223.

compositions on time, mass and temperature. Here a wide field is open to investigation, but numerous obstacles must be cleared away before its conquest can be accomplished. The results which have already been achieved in this direction clearly show that its cultivation will stamp its character on a new chapter of the development of scientific chemistry and that the period has arrived when the investigation of the Why? and the Wherefore? of the formation of new compounds will be the chief object of research, instead of the mere attempt to prepare such bodies.

XIV.

CHEMICAL ACTION OF LIGHT.

§ 268. Light which is nothing else than a form of radiant heat has the power of producing chemical changes, but only a limited number of substances are affected by its action.[1] Many oxides, chlorides, bromides and iodides which are stable in the dark are reduced by light, some give off free oxygen, chlorine, &c., but others are only decomposed when bodies are present which can combine with the liberated negative element. Light also has the power of producing compounds which are not formed in the dark. These reactions probably belong to the same category as the previous ones, for light acts on free chlorine and probably on free oxygen exactly in the same way that it does on chlorides, for it facilitates even if it does not effect the splitting up of the molecules into atoms.

The well-known formation of hydrochloric acid from its elements by the action of light, the chlorination of hydrocarbons, the decomposition of water by free chlorine with formation of hydrochloric acid, and the addition of chlorine or bromine to non-saturated compounds, such as carbon monoxide, ethylene, sulphurous anhydride, &c., all appear to be due to this cause, since the decomposition of the chlorine molecule must precede the act of combination.

$$*-CO-*+Cl-Cl=Cl-CO-Cl$$
$$H_2C=CH_2+Cl-Cl=Cl-CH_2-CH_2-Cl \text{ \&c.}$$

In this way all the effects of light may, like those of heat, be regarded as acts of decomposition or dissociation, followed by combination (*vide* § 208) and may therefore all be con-

[1] *See* Ad. Wüllner, *Lehrb. exp. Physik*, 1871, iii. 268; A. Naumann, *Gmelin-Kraut's Handb.* i. part 1, 823; E. Becquerel, *La Lumière, ses causes et ses effets*, ii. 1868.

sidered from the same standpoint. According to older ideas the effects of light were considered partly as acts of combination and partly of decomposition, that is to say, as reactions of precisely opposite nature.

§ 269. Only certain kinds of light can produce chemical changes; this power is confined to a distinct wave-length or colour. Only the blue, violet, or invisible ultra-violet rays, and to a less extent the green and yellow, act on most bodies. The red rays have scarcely any action. The decomposition of carbonic acid in the green organs of plants is caused more especially by red and yellow rays, and is scarcely affected by the more refrangible rays. There may be a few other changes of a similar nature.

Since the absorption of red and yellow rays by ponderable matter produces a greater rise in temperature than is caused by blue or violet rays, it might be concluded that the change is not due to the heating effect but to the light itself, *i.e.* the vibrations of the ether of definite wave-length. It is probable that different decompositions are caused by different kinds of coloured light. Each decomposition is specially but not exclusively due to a distinct colour. This connection appears to be closely related to the property which the elements possess when they are in the state of incandescent gases, of giving off light of a definite wave-length and of absorbing according to Kirchhoff's law [1] the same light and not allowing it to pass.

Bunsen and Roscoe [2] have proved by quantitative experiments that the chemical action of chlorine is produced by exactly that kind of light which it absorbs; for light which has passed through a sufficiently long layer of chlorine gas ceases to have any further action on chlorine. According to Morren [3] and Gernez [4] this light no longer contains any blue or violet rays. This clearly proves that the light as such is destroyed by its action and its kinetic energy is converted into other forms of energy.

[1] *Untersuchungen über das Sonnenspectrum und die Spectren der chemischen Elemente*, 2. Aufl., Berlin, 1862, 22.

[2] 'Photochemische Untersuchungen,' *Pogg. Ann.* xcvi. c. ci. cviii. and cxvii

[3] *Compt. Rend.* 1869, lxviii. 376. [4] *Ibid.* 1872, lxxiv. 660.

§ 270. In spite of the great practical value of the chemical action of light for photography and other branches of technical industry, few investigators have attempted exact quantitative measurements of its action. This is undoubtedly due to the great difficulty of the subject. The combination of hydrogen and chlorine under the influence of light has been investigated by J. W. Draper[1] and afterwards by more exact methods by Bunsen and Roscoe.[2]

Most of the other numerous researches on the chemical action of light are only qualitative, or treat of such complicated changes that in the present state of our knowledge it is only occasionally that any important theoretical result can be deduced from them.

§ 271. The quantitative measurements have shown that the action of light is not instantaneous. On the contrary it gradually develops and requires a considerable time before it attains its full strength. When a mixture of chlorine and hydrogen, which has been kept in the dark, is exposed to the light, there is either no hydrochloric acid, or only a very small quantity formed in the first moment: but the rate of formation increases so that the quantity formed in a given time, *e.g.* a minute, continues to increase until it attains a maximum which varies with the composition of the gaseous mixture and with the intensity of the light.

Bunsen terms this gradual increase in the action *Induction*. Induction depends on the composition of the gas, its mass and the intensity of the light. The rate of induction increases with the purity of the gas, and with the accuracy with which the constituents are mixed in their combining proportions. The rate of induction diminishes as the quantity of gas increases, but it is rapidly accelerated by an increase in the intensity of the light, so that in clear daylight instantaneous ignition and violent explosion may ensue.

Induction only takes place when the mixed gases are exposed to light; exposure of each gas separately to the light will not enable them to combine. On the other hand, if the

[1] *Phil. Mag.* 1843, xxiii. 401. *See* also the literature in Poggendorff's *Biogr. liter. Wörterbuch*, 1863 i. 601.

[2] *Loc. cit.*

gaseous mixture has been once exposed to the light, it will retain in the dark, for about half-an-hour, its capacity for forming hydrochloric acid in the light. If the gas has remained in the dark for a short period and is again brought into the light, it requires a very short period of induction; but the period of induction will be lengthened by keeping the mixture in the dark for a longer time. Exposure to the light renders the gaseous mixture capable of entering into combination, but it does not bring about combination itself. This condition loses its effect if it is not developed into combination by further exposure to the light.

Although in the case of chlorine and hydrogen it is only the mixed and not the separate gases which undergo induction, there are bodies, more especially certain silver salts, which on exposure to light acquire the property of being reduced by oxidisable bodies, by which they are either not decomposed or only very slowly decomposed in the dark. In most cases it is not necessary for the oxidisable body to be present when the silver salt is exposed to the light.

Silver chloride and iodide, exposed to the light on a photographic plate without any reducing action being visible when brought into a dark room and immersed in a solution of gallic acid or other reducing agent, are reduced at those points where they have been exposed to the light. The extent of the reduction increases with the intensity of the light.

Here one substance acquires the power, in the absence of the other, of combining with that other body in the dark, although in the case of chlorine and hydrogen the separate gases could not experience induction.

But there may not be any essential difference between the action of light on chlorine and on silver chloride. In both cases, light brings about a condition which facilitates the escape of the atoms from the molecule. The fact that this condition of the silver salt remains for a considerable time, whilst in the case of chlorine which is not mixed with hydrogen it ceases when the exposure to the light ceases, finds an analogy in the well-known fact that many bodies are phosphorescent, *i.e.* they have the power of absorbing the light which falls on them and giving it out again in the

dark, whilst others appear dark as soon as their exposure to the light ceases.

It has not yet been definitely proved in what this state of induction consists. But since this condition is brought about by vibrations of definite rhythm, by waves of light of definite colour, and as a certain amount of time is required for its production, there is scarcely any doubt that it will be found to consist essentially of vibrations or other periodical movements. This is rendered more probable by the observation of Roscoe and Bunsen that the slightest admixture of a third gas or even of a slight excess of chlorine or hydrogen exerts a very great influence on the action of the light. As the quantity of admixture is by no means commensurate with the great influence it exerts, the retarding action appears to be due to a disturbance or interruption of the regular rhythm of the movement. But we must not assume such a regularity in the motion as to cause each particle to behave exactly like the others, for in this case all the particles would simultaneously enter into that condition in which they would act on each other. On the contrary, we must assume a dissimilarity in the motion of the individual molecules, similar to that we have used for the explanation of a gradually increasing dissociation (§ 205).

§ 271. When the maximum of induction is attained, the quantity of hydrochloric acid formed in the unit of time remains constant, provided it is removed by water as soon as it is formed. The quantities formed in equal periods of time by light of different intensities are then proportional to the intensity of the light, or, to use a more correct expression, are proportional to the intensity of its active rays. But according to the undulation theory, the intensity of each colour is proportional to the square of the amplitude of vibration and inversely proportional to the time of vibration, hence it follows that the quantity of chlorine combined is proportional to the kinetic energy of the light employed ; consequently a definite quantity of energy is required for each molecule of chlorine. Hence it appears that not only is there an equivalence between heat and chemical change, but a similar relation also exists in the case of light.

The kinetic energy of the light which induces the combina-

tion of the chlorine and hydrogen to form hydrochloric acid has not been accurately measured, but it is very small in comparison with the expenditure of heat which is generally required to bring about a chemical change. It does not necessarily follow from this that a very feeble resistance is offered to the decomposition of the chlorine molecule, which is overcome by the action of light. It is quite possible that this decomposition is only effected by the peculiar movement of the chlorine atoms to which the light merely imparts a particularly favourable direction.

XV.

CHEMICAL CHANGE, AS CAUSE AND EFFECT OF ELECTRICITY; ELECTROLYSIS.

§ 272. Since Volta's discovery, no one has disputed the intimate connection between electricity and affinity; that cause of chemical change which is dependent on the material nature of the bodies taking part in the change. We are at the present time scarcely better informed as to the nature of this connection than we were at the beginning of this century, although an extraordinary number of facts bearing on this subject have been amassed in the meantime.

It has already been stated in § 108, that the views expressed by Humphry Davy[1] in the following words, possess the greatest degree of probability:

'Electrical effects are exhibited by the same bodies, when acting on masses, which produce chemical phenomena when acting by their particles; it is not, therefore, improbable, that the primary cause of both may be the same, and that the same arrangments of matter, or the same attractive powers, which place bodies in the relations of positive and negative, *i.e.* which render them attractive of each other electrically, and capable of communicating attractive powers to other matter, may likewise render their particles attractive and enable them to combine, when they have full freedom of motion.'

'This view of the possibility of the dependence of electrical and chemical action upon the same cause has been much misrepresented. It has been supposed that the idea was entertained, that chemical changes were occasioned by electrical changes; than which nothing is further from the hypothesis which I have ventured to advance. They are conceived, on

[1] *Elements of Chemical Philosophy*, H. Davy (vol. iv. of the collected works, section vii. paragraphs 33 and 34).

the contrary, to be distinct phenomena, but produced by the *same power* acting in one case on masses, in the other on particles.'

We now understand something more of the nature of electricity than was definitely known at that time. The notion that electricity is a fluid or that two such fluids exist was doubted by Davy and is now no longer credited. Davy called electricity 'a state or condition,' and we can now assume with a tolerable amount of certainty that electric conditions are states of motion of a peculiar form, which like all others obey the laws of the conservation and transformation of energy. But we do not know what form the movements characteristic of the electric state assume, nor do we even know whether the matter in motion is ponderable or imponderable. It is impossible for us to ascertain the relation between affinity and electricity, whilst these questions remain unanswered.

Although the connections between the immediate causes of chemical and electrical phenomena remain unknown, we have nevertheless made considerable progress since Davy's time in our knowledge of the relations existing between both kinds of phenomena, for which we are chiefly indebted to Davy's pupil and successor, Michael Faraday, in spite of the somewhat erroneous interpretations which he gave to certain of his observations.

§ 273. Electricity, like heat, appears not only as the cause but also as the effect of chemical change. When two bodies of different composition come in contact, an electrical separation always takes place, one body becomes positive and the other negative. This separation may be accomplished by contact at a single point, if the bodies are conductors, but if they are non-conductors, then every point on the surface of one body must be brought in contact (by friction) with one or more points of the other non-conductor. Volta's supposition that the electrical separation is caused by simple contact, has been frequently disputed, and it has been assumed that the production of the electricity is due to the chemical changes, such as oxidation, which the bodies undergo when in contact. The latter view, which is still held by some physicists, does not appear to the author in unison with certain facts. Without deciding this

difficult problem, we will assume that Volta's views are correct. The degree or tension of the electrical disturbance resulting from the contact of two heterogeneous bodies appears to be closely connected with their affinities. The stronger the affinity between the two bodies, the more powerful the tension will be.

The electro-chemical theory of Berzelius is based on this idea, a theory which materially contributed to the introduction of a systematic classification in Inorganic Chemistry, but has since been abandoned because the erroneous deductions drawn from this doctrine were not in unison with the phenomena of substitution observed in Organic Chemistry. The theory of Berzelius has fallen into oblivion. It is scarcely mentioned by new text books, and no attempt has been made to determine the position of some of the recently discovered elements in the series based on the differences in their electrical potential. Although we regret the complete abandonment of the once highly valued tenet of the celebrated discoverer, we cannot deny that it has never been anything more than a mere undeveloped hypothesis.

Berzelius considered that the electricity contained in the atoms was not only the source of the light and heat which accompanies their combination, but also the cause of their adhering together after combination. His own account of these views [1] acknowledges that this is a contradiction, which he is incapable of solving. This contradiction was but slightly felt, because Berzelius scarcely made any other application of his theory than the division of the elements into electropositive and electronegative, a classification we still retain. When he attempted a further application of his theory he fell into error, *e.g.* in his opposition to Faraday's [2] law of electrolytic equivalents and Dumas' theory of substitution, neither of them being in unison with his theoretical views, but both nevertheless perfectly true. Even at the present day the foundations for the erection of an electrochemical theory are not much firmer than they were at that period. We must therefore be very cautious in making theoretical speculations, and should confine ourselves closely to facts, if it were only

[1] Berzelius, *Lehrbuch*, 5. Aufl. 1843, i. 67. [2] *Ibid.* 100.

that one of our chief difficulties arises from the insecurity of our facts.

§ 274. Few direct measurements have been made of the separation of electricity, resulting from the contact of two heterogeneous bodies; the most careful experiments of R. Kohlrausch, Gerland, and Hankel[1] have shown how exceedingly difficult it is to obtain trustworthy results.

The slightest superficial oxidation of the metals, or the presence of moisture, or of small quantities of impurities in the metals, produces such great changes in their contact electricity that many physicists have denied the existence of contact electricity, and ascribed the fact that the bodies are charged with electricity to the chemical action of the oxygen or moisture in the atmosphere. Although this notion is too extreme, we can scarcely hope to obtain reliable measurements of contact electricity, even for the less oxidisable metals, not to mention the non-metallic elements and the oxidisable metals. But we may safely assume that the metals, and probably all chemical elements and many of their compounds, can be arranged in a so-called electric tension series, in which each body is electropositive toward any one higher in the list, and electronegative toward any one lower. The difference in electrical potential between any two metals is equal to the sum of the differences between all the intervening metals. Thus Kohlrausch found that

Zn | Fe = 74·7	Fe | Pt = 32·3
Zn | Pt = 106·4	74·7 + 32·3 = 107·0.

The difficulty of directly determining this difference in potential has led to the proposal to measure contact electricity indirectly. The two metals to be tested are placed in direct contact or are connected by a metallic conductor. They are then immersed in a decomposable conducting liquid, when the positive electricity flows through the metallic conductor to the *positive* metal. Here again the tension between A and C is equal to the sum of the tensions between A, B, and B and C.

[1] For résumé of experimental results, and the literature of the subject, *vide* Wiedemann's *Galvanismus*, i. (2nd edition), 21.

For example, Poggendorff[1] has shown that in dilute sulphuric acid

Zn | Sn	= 40·9	Sn | Cu	= 41·0
Zn | Cu	= 82·4	40·9 + 41	= 81·9

when the tension of a Daniell's element = 100.

This process generally yields the same tension series of the elements as is obtained by the direct observation of contact electricity; but the nature of the liquid exerts a certain influence, not only on the strength of the electrical disturbance, but also, under certain circumstances, on the position of the elements in the series. Potassium cyanide yields a different series from that obtained with dilute acids or alkalis. Different authors have obtained contradictory results with one and the same liquid. This is doubtless due to the greater or lesser degree of purity of the substances employed. Probably very few of the substances used were as pure as they might have been, and a large portion of them were doubtless very impure. Consequently the tension series exhibit discrepancies.[2]

But this process only permits of conductors of electricity being arranged in a series, and a part of these were, for various causes, unfit for experimental treatment; it was therefore necessary to seek for new methods in order to be able to arrange all the elements in such a tension series.

Observation shows that, as a rule, a positive element is separated from its combination with a negative element by a stronger positive, and a negative by a stronger negative element. The replacement of one element by another has been frequently used as a means of determining its position in the tension series. In its compounds with more positive elements, *e.g.* metals, iodine is replaced by chlorine, and in its compounds with the negative oxygen, chlorine is replaced by iodine. From these observations it is concluded that iodine is more positive or less negative than chlorine. The reversal of many reactions (*vide* Section 13) shows that deductions of this kind may be very erroneous.

It is not surprising that the tension series, which Ber-

[1] *Pogg. Ann.* 1845, lxx. 60; Wiedemann, *Galvanismus*, i. (2nd edition), 369.

[2] *See* Wiedemann, *Galvanismus* (2nd edition), i. 58.

zelius[1] drew up many years ago, embracing all the known elements from the most negative to the most positive, should contain some errors. The accuracy with which Berzelius has fixed the position of most of the elements is very surprising. With the exception of carbon and hydrogen, which he certainly placed too near the negative end of the series,[2] only an insignificant number of rearrangements are necessary, and these even at the present time cannot be accurately indicated.

§ 275. The preparation of a correct electric tension series embracing all the elements must for some time remain a desirable but an unaccomplished task. An easier and more immediately remunerative problem is the investigation of the different natural families of the elements in reference to their mutual electrical position, which has been previously mentioned (§§ 75, 76), and a comparison of the different families with one another. The following table indicates, as far as our imperfect knowledge permits, the observed or assumed electrical behaviour of the elements. The arrows are pointed towards the more positive element.

		Li	←	Be	←	B	→	C	←	N	←	O		F	→					
		↓		↓		↓		↑		↓		↓								
(F)	→	Na	←	Mg	←	Al	←	Si	←	P	←	S	←	Cl	→					
		↓		↓				↓		↓		↓		↓						
(Cl)	→	K	←	Ca	←	Sc	←	Ti	←	V	←	Cr	→	Mn	←	Fe	←	Co	←	Ni	←
	(Ni)	↰↳		Cu	↳↳	Zn	←	Ga	↓	—	←	As	←	Se	←	Br	↳↳		↑		↑
(Br)	→	Rb	↰↳	Sr	↰↳	Y	←	Zr	←	Nb	↓	Mo	↓	—	↓	Ru		Rh	→	Pd	→
	(Pd)	↳↳		Ag	↳↳	Cd	←	In	↓	Sn	←	Sb	↰↳	Te	←	J	→			↑	
(J)	→	Cs	↰↳	Ba	↰↳	La		Ce	↰↳	Ta	↰↳	W		—		Os	→	Ir	→	Pt	→
	(Pt)	→	Au	→	Hg	→	Tl	←	Pb	←	Bi	↓	—		—						
			—		—		Th		—		—		U		—						

Although this table is imperfect and uncertain, it gives rise to some considerations which supplement those in §§ 75 and 76. The variation of the electrochemical properties with the atomic weights mentioned in these sections exhibits the same periods as those shown in the table of atomic volumes. The elements from Li and from Na grow more and more negative until Fe and Cl are reached, when a positive maximum is suddenly attained. The same is true of the

[1] Berzelius, *Lehrbuch* (5th edition), i. 118.

[2] Carbon comes next to platinum, and hydrogen next to tin. *Vide* Bunsen, *Liebig's Annalen d. Pharm.* 1841, xxxviii. 311.

series beginning with K, Rb, and Cs, with this difference, that between each pair of light metals a heavy metal is introduced, and the less sharply defined positive maximum does not always occur in the same family, but is first exhibited by Zn and Cd, then by Pb or Tl, and afterwards by Hg. Other small maxima also appear at C, if B is really more negative; then in the iron group, Mn, Fe, Co, Ni, which are more positive than Cu.

If we regard each family by itself, we often find that the higher the atomic weight the more strongly positive the element will be. This is the case in the following groups:—

$$- \left\{ \begin{matrix} \text{N}, & \text{P}, & \text{As}, & \text{Sb}, \\ \text{O}, & \text{S}, & \text{Se}, & \text{Te}, \\ \text{Fl}, & \text{Cl}, & \text{Br}, & \text{I}, \\ \text{Li}, \text{Na}, & \text{K}, & \text{Pb}, & \text{Cs}, \end{matrix} \right\} +$$

It may also be true of the following groups, although Bunsen[1] found Sr to be negative towards Ca; and up to the present time it has not been proved that Si is positive towards C.

Be,	Mg,	Ca,	Sr,	Ba,	
B,	Al,	Sc,	Y,	La,	Yb,
C,	Si,	Ti,	Zr,	Ce,	Th.

This order is reversed in the groups of the more or less malleable metals:

$$+ \left\{ \begin{matrix} \text{Fe}, & \text{Ru}, & \text{Os}, \\ \text{Co}, & \text{Rh}, & \text{Ir}, \\ \text{Ni}, & \text{Pd}, & \text{Pt}, \\ \text{Cu}, & \text{Ag}, & \text{Au}, \\ \text{Zn}, & \text{Cd}, & \text{Hg}, \end{matrix} \right\} -$$

Probably also Ga, In, Tl.

On the other hand, Sn is negative towards Pb.

The connection between atomic weight and electrical properties is merely conjectural in the case of

V,	Nb,	Ta,	
Cr,	Mo,	W,	Ur.

[1] *Ann. Chem. Pharm.* 1855, xciv. 110.

These relations show that it would be remunerative to make the behaviour of the different families the subject of a new investigation, in which perfectly pure materials and one uniform method should be employed. Such an investigation would probably cast more light on the subject than many of the former experiments, which were made with impure material, and are, from a chemical point of view, utterly valueless.

§ 276. The finite cause of the development of electricity by contact doubtless lies in the difference in the material nature of the bodies in contact. But so long as we are ignorant of the true nature of electricity we cannot hope to offer a satisfactory explanation of its production by contact. It was formerly assumed that the separation was brought about by the powerful attraction which the ponderable masses exert on what we call electricity; in this way one body received an excess of positive electricity, and the other an excess of negative electricity. The two forms of electricity mutually attract each other, and a state of equilibrium ensues, when the two attractions are equally powerful. Although the existence of such an attraction between electricity and matter is not exactly denied at the present time, it is nevertheless very difficult to form a clear idea of the nature of such a force acting between ponderable matter and a form of motion. Still we do know that the molecular energy contained in the bodies in the form of heat plays an essential part in this electrical separation, in the passage of electricity from one body to another. Not only does contact electricity vary considerably with the temperature, but the movement of the electricity through the terminals is accompanied in one direction by an absorption, and in the other by a liberation of heat.

This phenomenon, which was discovered by Peltier, can only be observed when the electric current has passed for a short time through the terminals, but there is no doubt that it also takes place in the electrical separation, which is instantaneously produced by contact. We may, therefore, assume that a portion of the molecular motion at the terminals is converted into electrical motion by the contact of heterogeneous bodies. It is a matter of opinion whether it really is necessary to assume that there is an attraction between matter

and the form of motion which we call the electrical condition, or whether it would not be sufficient to assume that on contact the different kinds of motion of heterogeneous matter mutually destroy each other, and in this way produce that state which we term an electrical separation.

§ 277. It is obvious that the contact of heterogeneous substances can only produce a state of equilibrium, and not a continuous electrical movement. If this were not the case, it would create an inexhaustible source of energy, perpetual motion. If the equilibrium is disturbed, it at once endeavours to re-establish itself. The electricity moves as long as the disturbance lasts. If the latter is maintained, then the motion of the electricity continues as an electric current. This involves a continuous expenditure of energy, by which the electricity is moved in opposition to the forces tending to re-establish the state of equilibrium.

One condition for the development of such a current is the presence of a continuous circuit composed of conductors. This of itself is incapable of creating a current. If it is entirely composed of conductors of the first order, all having the same temperature, no current is formed, but a state of rest results, in which the forces acting on a given electric particle in any part of the circuit maintain a state of equilibrium, so that the electricity is everywhere at rest.

This state is mathematically defined as the potential or tension of the electricity. This state of equilibrium can be disturbed in two ways, by heating or cooling one of the contact surfaces, or by the introduction of a conductor of the second order, *i.e.* a body which conducts but is at the same time decomposed by electricity. In the first case a Seebeck's or thermo-electric current is produced, and in the latter a galvanic current results.

According to the contact theory the thermo-electric current is due to the fact that the potentials of different substances, and consequently the forces acting on an electric particle within their mass, are affected to different extents by the temperature; hence the difference between these potentials at the points of contact also changes.

In the simple case of a ring formed of only two metals

soldered together, equilibrium is only possible when both junctions have the same temperature, and therefore tend to produce one and the same difference of tension. If the temperature at one junction changes, then a change in the electrical separation at this point will occur, which will extend over the whole of the metal till it reaches the other junction. But here the electrical separation no longer corresponds to the state of equilibrium; consequently, a portion of one of the electric fluids will pass the boundary, and in this way prevent either of the junctions resuming its state of equilibrium.

Such a ring may be compared to a water conduit, divided into two parts by weirs of different heights. Whatever volume of water is pumped above the top weir will always flow down to the lower, and a state of rest will not ensue. But work at the pump is necessary to maintain this constant movement of the water, and the same is true of electricity. The energy required to maintain the flow of electricity is derived from the heat imparted to the warmer junction. This junction is cooled by the current, the other is heated; so finally a state of equilibrium is again established. If the current is to be continuous, heat must be continually imparted to one point of contact and withdrawn from the other.

One might be tempted to believe that the connection between the material nature of the substances and the forces exciting the electricity would be clearly exhibited in these currents which are solely produced by contact and by heat. This is, to a certain extent, the case, but a systematic relation of this nature with the chemical composition of the substances cannot be established.

The most powerful currents are in some cases produced by substances which exhibit a great similarity in their chemical behaviour, and in their position in the ordinary tension series. The positive current passes across the heated junction from the negative substance to the positive. If all the bodies are arranged in a continuous series, from the most strongly negative to the most strongly positive, a thermo-electric series is obtained which differs widely from the ordinary tension series; *e.g.* bismuth stands at the extreme negative end of the list, and antimony, which is closely related to the former

metal, is found at the extreme positive. Cobalt and nickel are negative, iron positive, and so on.

It is true that experiments show that the presence of very slight impurities or differences in the structure of the metals materially affects their position.[1] Even if this remarkable behaviour is in many cases due to the presence of impurities, this cannot always be the cause. The absence of a clear relation between the nature of the bodies and the strength of their thermo-electric currents is perhaps chiefly due to the fact that the latter does not depend on the absolute values of the potential of the different forces acting on the electricity in the different substances, but depends only on the value of the variation of these forces with the temperature, which need not stand in any simple relation to the chemical nature.

Perhaps the views of F. Kohlrausch [2] on the production of the thermo-electric current are to be preferred. He considers that the current is not exactly due to contact, but that each movement of heat is transformed to a certain extent into an electrical movement, and *vice versâ*. The electromotive force of a thermopile depends essentially on the resistance of both the conductors. Whatever our theoretical views of the cause of the thermo-electric current may be, it is the disturbance of the equilibrium of the temperature which causes the disturbance of the electrical equilibrium. Since both depend on the material nature of the bodies, we must succeed at some future period in ascertaining more clearly the nature of this connection.

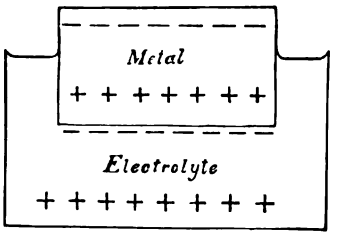
§ 278. The other mode of disturbing electrical equilibrium, which consists in the introduction of a conductor of the second class, is intimately connected with the material nature of the bodies. All the conductors of this class are compound substances, and therefore capable of decomposition; most of them are liquids, some are semi-liquid, or solid, but not so rigid as to preclude a certain mobility of their particles. They are characterised by the fact that when they conduct a

[1] Wiedemann, *Galvanismus*, i. (2nd edition), 804.

[2] *Pogg. Ann.* 1875, clvi. 601. *Vide* also Clausius, *Die mechanische Wärme Theorie* (2nd edition), ii. 1879, section 7; *Die Thermoelektrischen Ströme*, 177 and 337.

voltaic current they are themselves decomposed, and that their conductivity increases with the temperature,[1] whilst the conductivity of conductors of the first class, which are not decomposed, diminishes with the temperature.[2] The conductors of the second class are termed *Electrolytes, i.e.* bodies decomposable by electricity.

An electrical separation is brought about by the contact of an electrolyte with a metal, or any other conductor of the first class. This takes place whether the metals are noble or base, whether they are attacked or not attacked by the electrolytes. As a general rule the metal becomes negative, and, the more strongly negative, the nearer it is to the positive end of the tension series. For example, in water, zinc is more strongly negative than copper, and in dilute acids zinc, iron, and copper are electrically negative, and gold and platinum positive. This peculiarity of their behaviour has not yet been thoroughly explained; but there is no doubt that the metals, especially those which are strongly positive, attract the negative constituent of the electrolyte O, Cl, &c. The result of this attraction may be that the portions of the electrolyte which are in contact with the metal are either decomposed, or at any rate arranged in such a way that the negative constituent is directed towards, and the positive from the metal. Probably a condition of things is brought about similar to that existing in the Leyden jar or Franklin's plate. At the contact surface a layer of negative electricity in the electrolyte is opposed to a layer of positive electricity in the metal. The quantities of the opposite electricities simultaneously excited by this separation are distributed over both substances, the negative through the metal, and the positive through the electrolyte, as is shown by the accompanying diagram. When two metals are immersed in the same liquid, each is excited in its own peculiar fashion, but in addition the electricity excited by the other



[1] Ohm, *Pogg. Ann.* 1844, lxiii. 403.

[2] Faraday, *Phil. Trans.* 1821, 431; *Gilb. Ann.* 1822, lxxi. 241.

metal in the liquid also extends to it, so that its final condition is represented by the sum of both. When zinc and copper are separately immersed in water or dilute sulphuric acid, each metal will be negative, the zinc more strongly than the copper, the electrolyte will be positive. But if both metals are immersed in the same liquid, then the positive electricity from the zinc passes on to the copper, and is partly neutralised by its negative charge, so that only the positive excess remains; and in the same way the positive charge in the liquid, which proceeds from the copper, passes on to the zinc and diminishes without destroying its negative charge. A state of equilibrium cannot exist when the positive copper is in contact with the negative zinc, because the contact of the metals tends to make the copper negative and the zinc positive, whilst contact with the liquids tends to reverse this condition.

In this way an electric current is produced in which the positive electricity circulates from the copper through the metallic contact to the zinc, and from this through the electrolyte back to the copper.

This combination of substances for producing a current is termed a galvanic element.

§ 279. The current produced by an element of this description differs from a thermo-electric or an induced current which flows through a circuit entirely composed of conductors of the first class. The chief point of difference is that the current in passing from the electrolyte to the metal liberates the constituents of the electrolyte which are termed *ions*. The constituent liberated at the positive pole is termed an *anion*, that at the negative pole a *cation*. In the same way, the conductor of the first class, by which the positive electricity enters the liquid, is termed an *anode* and that by which it leaves it a *cathode*. They are both called *electrodes*. The anion is electronegative towards the cation. We can also say that a positive *ion* flows in the direction of the current with positive electricity, the negative *ion* flows in the opposite direction.

As the ions are classed in the tension series, their separation at the electrodes causes polarisation, *i.e.* a current moving in a contrary direction to the ordinary current. This weakens and finally destroys the original current, so that a state of electrical equilibrium is established.

The difference between a combination of substances embracing one or more electrolytes and one composed entirely of conductors of the first class is not due to the impossiblity of establishing equilibrium in the former case, but it arises from the fact that equilibrium can only be established by the liberation of the ions at the electrodes. It is only when the polarisation of the electrodes is partially or wholly prevented that a state of equilibrium is not established, and then the electricity circulates continuously, and fresh quantities of the *ions* are continually carried to the electrodes. There are two different methods of preventing polarisation, which are generally used simultaneously. It is prevented at the cathode by making this of the same substance as the cation which is deposited on it, so that no new body is introduced by this deposition. The anode, or that portion of the electrolyte which surrounds it, is made of a substance which will unite with the anion and render it harmless.

In this way we obtain a constant galvanic element. Its current will continue so long as material lasts which hinders its polarisation, *i.e.* the equilibrium.

§ 280. Since the movement of the electricity and of the ions meets with resistance, *e.g.* friction, their continuous movement demands an expenditure of energy to overcome this resistance. This energy is imparted by the chemical changes in the electrolyte, destroying or preventing the polarisation; generally by oxidation or some analogous process taking place at the anode. Instead of heat which these changes generally produce, they furnish in this case the force necessary for the movement of the electricity and the ions. Fresh quantities of the electrolyte are continually decomposed, and its constituents carried to the electrodes; further the electricity is continuously moving through the whole circuit, not only through the metallic portion of the circuit but also through the electrolytes. The portion of the force which is used for circulation of the current again appears in the circuit as heat, unless it is spent in other work. That portion used for liberating the ions can only be regained by the recombustion of the ions.[1]

[1] Julius Thomsen, *Wiedemann's Ann.* 1880, xi. 246; *Journ. f. pr. Chem.* N.F. 1880, xxi. 73.

We may therefore say that the current of a galvanic element is maintained by the chemical changes taking place in it. The view formerly held by many celebrated physicists that the current is originally produced by these changes is erroneous. The chemical change in the cell of a galvanic element which prevents polarisation acts in the same way as the heat imparted to the junctions of a thermopile : it destroys the electrical equilibrium.

§ 281. The intensity of the current, that is, the amount of electric force which flows through any given section of the circuit in the unit of time, depends on the dimensions and on the nature of the conductors forming the circuit. According to Ohm's law the intensity is inversely proportional to the resistance, and the latter can be directly determined by experiment. The resistance R is inversely proportional to the conductivity κ (which is a constant depending on the nature of the conductor). It is also inversely as the section ω and directly as the length of the conductor λ.

$R = \frac{\lambda}{\kappa\omega}$, or if the circuit is composed of different conductors, $R = \frac{\lambda_1}{\kappa_1\,\omega_1} + \frac{\lambda_2}{\kappa_2\,\omega_2} + \frac{\lambda_3}{\kappa_3\,\omega_3} + \ldots$.

If the resistance remains constant, different combinations do not produce the currents of the same, but of very different intensity, according to the nature of the substances in contact. Hence it is necessary to assign a definite electromotive force to each combination. This can be directly measured by the difference in the electrical tension of the free ends of the broken circuit, but it is generally calculated from two other values which can be experimentally determined, viz. the intensity and the resistance. It is proportional to both.

$$E = I.R.$$

This equation is generally given as $I = \frac{E}{R}$, or $I = \frac{\Sigma E}{\Sigma R}$, where Σ indicates that all the electromotive forces in the circuit are to be added together, and also all the resistances.

It follows from this law that the intensity of a current has a twofold dependence on the nature of the substances,

because their nature determines both the resistance and the electromotive force. Both these influences exerted by the substance can be separately determined, since the resistance depends on the dimensions of the body, but the electromotive force does not. Although these relations are very simple, confusion was frequently caused in former days by ignoring them in considering the connection between the intensity of the current and the chemical nature and affinity of the substances.

The relation between the atomic weight of the elements and their conductivity has already been discussed in § 74. The conductivity of compounds will be considered presently.

§ 282. The electromotive force of a combination of conductors of the first and second class is by no means a simple value. Since the current results from the simultaneous action of forces tending to establish equilibrium, *i.e.* polarisation, and forces tending to destroy it, the consequence is that the electromotive force varies with each of these forces. The process which produces or tends to produce polarisation, *i.e.* the decomposition of the electrolyte, has this peculiarity, that the electricity flowing through the electrolyte is proportional to the quantity of the ions liberated at the electrodes. Every atom of an element liberated at the electrode brings with it a definite amount of electricity, negative electricity at the anode, positive at the cathode. The amount of electricity depends solely on the chemical equivalence of the atom: this is also true of ions composed of groups of atoms or radicals. A monovalent atom or radical, under all circumstances, brings with it one and the same quantity of electricity. This is independent of the nature of the atom and the circumstances attending its liberation. A divalent element or radical brings with it twice as much, and a trivalent treble the quantity.

If the experiment is so arranged that the polarisation is at once destroyed and the liberated ions removed by chemical action, then we shall require for this purpose, such quantities of the necessary substances as will be equivalent to the liberated ions.

In an element composed of amalgamated zinc, platinum and dilute sulphuric acid, H_2 is liberated at the platinum

together with a definite quantity of positive electricity, the residue SO_4 of the acid appears at the zinc, and parts with O and an equivalent quantity of negative electricity. If these ions remain at the electrodes, polarisation and finally a state of equilibrium will ensue. The oxygen, however, oxidises the zinc and the oxide dissolves, forming sulphate, or what comes to the same in the end, the SO_4 unites with the zinc to form $ZnSO_4$, and if the platinum is surrounded by nitric acid, the H_2 is oxidised to H_2O. As a definite quantity of + E passes from the electrolyte to the Zn and the equivalent quantity of − E to the Pt, we have the following equivalent decompositions—

$$H_2SO_4 = H_2 + SO_4$$
$$SO_4 + Zn = ZnSO_4$$
$$H_2 + O = H_2O,$$

and for a Daniell's battery

$$H_2SO_4 = H_2 + SO_4$$
$$SO_4 + Zn = ZnSO_4$$
$$H_2 + CuSO_4 = H_2SO_4 + Cu.$$

The first and third equation may be replaced by a single equation, viz. $CuSO_4 = SO_4 + Cu$. The passage of electricity from one electrode to the other is associated with the liberation of the ions, each equivalent of the latter is always accompanied by the same quantity of electricity. If no secondary action takes place in the electrolytes, *i.e.* no other chemical change than that which serves to maintain the current, then there will be a complete equivalence between these decompositions and the passage of electricity from one metal to the other. It is, therefore, possible to determine the electricity quantitatively if we take as unit the amount of electricity which is transported by a monovalent atom: or double the quantity may be taken as the unit, a double atom of hydrogen, or a single atom of oxygen or any other divalent atom. This corresponds to the old equivalent of Berzelius. The latter unit has certain practical advantages, as many of the ions are divalent and calculations with half-atoms are inconvenient.

Although the quantity of voltaic electricity depends only on the number, and not on the nature, of the equivalents of

the electrolyte which is decomposed, nevertheless the influence which the nature of all the bodies forming the circuit exerts on the electromotive force of the combination is perceptible in the rate with which the movement takes place. Since this also depends on the resistance which is offered to the movement of the electricity as well as to the movement of the ions, it is necessary that the latter should be determined by experiment and eliminated. The product of the resistance into the intensity of the current gives the electromotive force, *i.e.* the accelerating force acting on the electricity and the ions.

§ 283. The electromotive force of a galvanic combination of conductors of both classes increases with the strength of the forces effecting electrical separation, and also with the rapidity with which the tendency to polarisation is destroyed. That is to say, it increases with the activity of the chemical changes of the conductors of the second class, and also with the distance which separates the conductors of the first class in the tension series.

As the expenditure of force required for the movement of the electricity and the ions is supplied by the chemical changes in the electrolyte, we may assume that under similar conditions the amount of electricity will increase with the amount of work done by these chemical changes and the amount of heat they can produce. Now Joule [1] has shown by experiment that the chemical changes taking place in the cell of a galvanic element evolve less heat than they are really capable of producing. The difference is equivalent to the work required for the movement of the electricity through the metallic conductors. This portion which is not liberated in the cell overcomes the resistance of the metallic circuit, and appears here in the form of heat.

On the assumption that the resistance of the cells is very small in comparison with that of the metallic conductors (an assumption which is not always correct), Sir William Thomson [2] arrived at the conclusion that 'the intensity of an electrochemical apparatus is, in absolute measure, equal to the

[1] Joule, *Phil. Mag.* [3] 1841, xix. 260.

[2] 'On the Mechanical Theory of Electrolysis,' by Sir W. Thomson, *Phil. Mag.* [2] 1851, ii. 434.

mechanical equivalent of as much of the chemical action as goes on with a current of the unit strength during a unit of time.' J. C. Maxwell[1] expresses this view as follows: 'The electromotive force of an electrochemical apparatus in absolute measurement is equal to the chemical action of an electrolytical equivalent.' The electromotive force of any combination can therefore be calculated from the thermic effect of the chemical change which takes place in the conversion of an electrochemical equivalent.

Julius Thomsen[2] confirmed these theoretical deductions for different galvanic elements in his thermochemical researches.

In a Daniell's element in which copper sulphate is decomposed and zinc sulphate formed, the total thermic effects for the double equivalent are, according to Thomsen—

$$(Zn, O, SO_3Aq) - (Cu, O, SO_3Aq) = 106090 - 55960 = 50130^c.$$

If cadmium replaces the copper, then we have

$$(Zn, O, SO_3Aq) - (Cd, O, SO_3Aq) = 106090 - 89500 = 16590^c.$$

Now 50130 : 16590 = 1 : 0·33, and the electromotive forces of these two combinations stand in this relation to each other.[3] Experimental results also confirm the theoretical deductions for a series of other galvanic elements.

Thomson's[4] hypothesis is not universally applicable. Joule's experiments prove that its application is limited by the nature of the metals in contact with the electrolytes. W. E. Ayrton and J. Perry[5] have also pointed out exceptions to this law.

Helmholtz[6] has recently proved, from the fundamental principles of the mechanical theory of heat, that Thomson's law is incorrect, because only a portion of the energy (termed free energy) produced by the chemical change is used in maintaining the current. He also pointed out the existence of galvanic elements of considerable electromotive force in

[1] *A Treatise on Electricity and Magnetism*, 1873, i. 316.

[2] *Journ. f. prakt. Chem.* [2] 1880, xxi. 73.

[3] S. J. Regnauld's determination, *Wiedemann*, loc. cit. 386.

[4] *Loc. cit.* 432 note.

[5] *Phil. Mag.* [5] 1881, xi. 43.

[6] 'Die Thermodynamik chemischer Vorgänge,' *Berl. Akad. Ber.* v. Feb 1882; *Math. Nat. Mittheil. Sitz.-Ber.* 1882 p. 7; *Chem. Centr.* 1882, 700, 703

which the sum of all the thermic effects is either zero or a negative quantity.

This was followed by an exhaustive series of experiments by F. Braun,[1] who proved that J. Thomsen's experimental confirmation of the law is only apparent. In the elements investigated, especially in the Daniell, the differences of the free energies of the changes taking place in the element are nearly equal to the differences of the total thermic effects; but in other galvanic combinations these differences are by no means equal. The electromotive force is sometimes larger and sometimes smaller than it should be according to Thomson.

That his law is incorrect is plainly evinced by the well-known fact that galvanic combinations in which the same chemical changes are taking place may have widely different electromotive forces.

For example, in any combination of zinc, sulphuric acid, and a more negative metal, the chemical change is—

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

Thomsen has shown that the thermic effect of this change is—

$$(Zn, O, SO_3Aq) - (H_2, O) = 106090 - 68360 = 37730^c,$$

and therefore the electromotive force is 0·75D, *i.e.* three-fourths the EMF of a Daniell.

This force varies according to the nature of the second metal. For example, according to Poggendorff's determinations—

$$Zn \mid Sn = 0{\cdot}41D \quad Zn \mid Cu = 0{\cdot}83D \quad Zn \mid Pt = 1{\cdot}43D.$$

If the zinc is amalgamated the EMF increases by 0·12 D in each of the three combinations without any alteration in the chemical changes in the electrolyte.

In each of these three combinations the amount of electricity transferred for each equivalent of hydrogen is obviously the same. The only difference is in the rate at which the electricity is transferred. If all the resistances are equal the

[1] *Wied. Ann.* 1877, v. 182; 1882, xvi. 561; xvii. 593.

intensities of the currents are inversely proportional to the times required for the transference of the same equivalents.

For the combinations

$$Zn, H_2SO_4, Sn; \quad Zn, H_2SO_4, Cu; \quad Zn, H_2SO_4, Pt$$

these times are as

$$\frac{1}{0{\cdot}41} = 2{\cdot}44 : \frac{1}{0{\cdot}83} = 1{\cdot}20 : \frac{1}{1{\cdot}43} = 0{\cdot}70.$$

As the negative metal takes no part in the chemical changes this difference can only proceed from the different strength of the electrical disturbance resulting from the contact of the different metals with zinc and the electrolytes. This fact can hardly be explained by the purely chemical theory of the electric current, which rejects the idea of contact electricity. It furnishes a very powerful argument in favour of contact electricity, and must be regarded as a proof of the correctness of Volta's theory.

§ 284. The chemical change in the electrolyte supports the electric current by destroying polarisation, and, on the other hand, the electric current, whatever its origin, decomposes an electrolyte introduced into its circuit. The same laws govern this decomposition, known as electrolysis, which govern the flow of electricity (accompanied by chemical change) through the cell of a galvanic element. The current of electricity traverses the electrolyte, and at the same time splits it up into two constituents, the *ions*, with which it appears at the electrodes. According to Faraday's discovery, each equivalent of any given ion is always accompanied by the same quantity of electricity at the electrodes. Hence it follows that when one and the same current passes through a series of electrolytes it decomposes equivalent quantities of the electrolytes. As previously mentioned in § 4, Faraday's law can be employed for determining the equivalent weights [1] of the elements and their compounds. If the ions enter into a secondary reaction by acting on the electrodes or the constituents of the liquids surrounding them, the products of these reactions are of course equivalent to the quantities of the ions and to the electricity.

[1] Not atomic weights.

The quantity transferred by an atom of hydrogen or other monovalent atom is taken as the unit. In electrolysis as in ordinary chemical reactions, a substance may possess different equivalent values; this is especially true of the metals. Copper and mercury are monovalent in the cuprous and mercurous salts, but divalent in the cupric and mercuric compounds. In the latter case their atoms carry with them twice as much electricity as they do in the former. The electrolytic equivalent is not an invariable property of the atom, but it is a condition which varies with the nature of the compound. This change of equivalence is not, however, of frequent occurrence.

§ 285. It is obvious that all electrolytes are compound substances; but every compound is not an electrolyte. Compounds may be divided into three classes: (1) conductors of the first class, which are not decomposed by the current; (2) conductors of the second class, or electrolytes; (3) non-conductors. The particular class to which a given substance belongs depends on its chemical nature and composition, and also on its physical properties, more especially on its state of aggregation. One and the same body in different physical conditions may belong to different classes.

The influence of physical condition is exhibited by many elements capable of existing in different allotropic modifications. The metallic variety is a conductor of the first class; the other modifications are non-conductors. The diamond, colourless phosphorus, and amorphous selenium are non-conductors; graphite, crystallised red phosphorus, and crystalline selenium[1] are conductors of the first class. Cinnabar (red HgS) is a non-conductor, but the isomeric black sulphide HgS is a fairly-good conductor of the first class.

Many bodies which are non-conductors in the solid state are electrolytes in a molten condition, *e.g.* Ag_2S, Cu_2S. Glass and other compounds are electrolytes before melting, as soon as they begin to soften.

Some compounds which are in the solid state conductors of the first class appear to act as electrolytes at a higher temperature. At any rate, Buff[2] has shown that many oxides and

[1] Hittorf, *Pogg. Ann.* 1851, lxxxiv. 218. [2] *Liebig's Ann.* 1859, cx. 288.

sulphides, such as MnO_2, Cr_2O_3, Fe_2O_3, Fe_3O_4, FeS_2 PbS SnO_2, which are conductors of the first class, behave like electrolytes, inasmuch as their conductivity increases instead of diminishes with an increased temperature (§ 278). It is possible that some of these compounds belong to the same category as Ag_2S, PbF_2 and HgI_2, which Faraday regarded as conductors of the first class. Hittorf[1] and Beetz[2] have shown that these bodies are electrolytes and undergo decomposition. But as it has not been definitely proved that the decomposition is equivalent to the intensity of the current, the question still remains undecided whether one and the same body can be an electrolyte and a conductor of the first class. Many asserted cases of double conductivity have proved on examination non-existent.

§ 286. The chemical nature and composition of the substance exert a great influence on its behaviour.

All compounds whose constituents are 'metallic' conductors are also conductors of the first class; viz. all alloys composed of the metals,[3] or of the semi-metallic elements.[4] Alloys containing Bi, Sb, and As, and also those containing the phosphorus and nitrogen metals, are, as far as they have been investigated, conductors of the first class.[5]

The tellurium and selenium metals also belong to this class.

On the other hand, those compounds are non-conductors which are entirely composed of non-conducting elements, *e.g.* chloride of iodine, bromide of iodine, chloride of sulphur, &c.

Compounds of conductors and non-conductors are found in each of the three classes. But no compound of the family VII. B.—*i.e.* of the elements Cl, Br, I, Fl—has been definitely proved to be a conductor of the first class. According to Faraday, HgI_2 and $PbFl_2$ belong to this class, and so does $PbCl_2$, according to Buff;[6] but the first two compounds have been proved to be electrolytes (see § 285), and Kohl-

[1] *Pogg. Ann.* 1851, lxxxiv. 20. [2] *Ib.* 1854, xcii. 457, 461.
[3] E. Obach, *Pogg. Ann.* 1875, Supplement, vii. 280.
[4] E. Elsässer, *Wied. Ann.* 1879, viii. 455.
[5] *E.g.* molybdenum phosphide, Wöhler, *Lieb. Ann.* 1859, cix. 374.
[6] *Loc. cit.* 285.

rausch[1] has shown that the conductivity of AgCl, AgBr, and AgI, even in the solid state, increases with the temperature, as is the case with all electrolytes. Oxides and sulphides occur in all three classes.

Only the halogens Fl, Cl, Br, I, and both the first members of the adjacent family in the natural system (§ 61), viz. O and S, form electrolytic compounds.[2] Bodies which do not contain any of these six elements are not decomposed by the current. They are, as a rule, conductors of the first class.

Whether the compounds which these six elements form with other elements are electrolytes or no depends on the nature of the other constituents, and partly also on the number of atoms in the compound. It is difficult to discriminate clearly between these influences; consequently too great a stress was formerly placed on the influence of the number of atoms contained in the compound.

Before any distinction was drawn between monovalent and divalent elements, it was believed that only those compounds can be electrolytes which are composed of an equal number of atoms of their positive and negative constituents. This rule is no longer applicable, since the majority of these compounds, such as the oxides of monovalent metals and the chlorides of divalent metals, are supposed to contain two atoms of one element to one of the other. It has also been proved that the chlorides of trivalent metals, such as Al, Ce, La, Di, are electrolytes. If bodies of the composition RCl, RCl_2, RCl_3, R_2O, and RO are electrolytes, it can no longer be assumed (as Hittorf[3] has already pointed out) that only diatomic compounds, *i.e.* composed of only two atoms, RCl, RO, possess this property.

There are certainly some chlorides of the formula RCl_3 which are non-conductors. But others of the type RCl_3 or R_2Cl_6 are electrolytes. So that the difference arises from the

[1] *Wied. Ann.* 1882, xvii. 642.

[2] Bleekerode (*Wiedemann's Ann.* 1878, iii. 167 and 174) calls some nitrogen compounds, *e.g.* hydrocyanic acid, ammonia, *good* conductors. According to Hittorf (*ibid.* iv. 412) and Kohlrausch (*ibid.* vi. 165) this is hardly justifiable.

[3] *Pogg. Ann.* 1858, ciii. 55; 1859, cvi. 566.

nature of the elements rather than from the composition of the compounds. Only a few elements are known which form two classes of compounds with negative elements; the compounds poor in negative elements are electrolytes, *e.g.* $SnCl_2$, $PbCl_2$, and the compounds containing a larger number of the negative atoms are non-conductors.

It is obvious that an electrolyte need not of necessity have a very simple composition, since many acids and salts, *e.g.* carbonates, silicates, nitrates, phosphates, sulphates, chromates, chlorates, and the salts of the alkaloids, which are composed of a large number of atoms, are electrolytes.

It is a remarkable fact that many bodies in the pure state, and therefore apparently under the simplest conditions, are non-conductors; but become when mixed with other non-conductors good electrolytes. Aqueous, alcoholic and ethereal solutions of different salts and acids are electrolytes; but pure water, alcohol and ether are non-conductors. Many of the salts are non-conductors, although their solutions are electrolytes. F. Kohlrausch [1] maintains that no simple unmixed substance is an electrolyte [2] at the ordinary temperature. It only becomes an electrolyte at a higher temperature, or in the presence of other bodies. These facts indicate that an electrolyte need not necessarily have a very simple constitution.

§ 287. The connection between the electrolytic property of a compound and the chemical nature of its constituents is difficult to determine, because the physical properties which influence the electrolytic decomposition vary with the composition of the body. It is often questionable whether it is the composition of a given compound, or perhaps the unsuitable state of aggregation it is in, which prevents its decomposition by the current. Nevertheless, it will not be uninteresting to take a general view of the behaviour of the most important compounds of the six elements which form electrolytes.

These six elements, F, Cl, Br, I, O, S, as well as their compounds with each other, are, in the pure, unmixed state, non-conductors. This has been proved in the case of liquid

[1] *Pogg. Ann.* 1876, clix. 271.

[2] According to Bleekerode (*loc. cit.*), hydrocyanic acid and ammonia are exceptions to this rule.

chlorine, bromine, iodine, and iodine chloride and bromide,[1] and for the oxides of sulphur SO_2 and SO_3.

The compounds of these six elements with hydrogen, HF, HCl, HBr, HI, H_2O, H_2S, are all non-conductors in the liquid form, if each is examined separately and unmixed with the others.[2] Mixtures of the first four compounds with the fifth compound, water, are very good electrolytes; an aqueous solution of sulphuretted hydrogen, H_2S, conducts much better than pure water, but about 3,000 times worse than aqueous hydrochloric acid.[3]

The fact that mixtures of halogen acids with water are good electrolytes is perhaps due to the formation of such compounds as $H_2OCl = HCl + H_2O$.

Julius Thomsen[4] has pointed out the probable existence of these compounds.

§ 288. The chlorides,[5] bromides, &c., of the groups of the light metals—

I. A : Li, Na, K, Rb, Cs.
II. A : Be, Mg, Ca, Sr, Ba.
III. A : —, Al,[6] [Sc], [Y], La, Ce, Di,[7] [Yb],[8]

are, in the molten state, good electrolytes, and serve for the preparation of these metals.

Their aqueous solutions are also good electrolytes.

They decompose thus: R | Cl, R | Cl_2, R | Cl_3.

As the metals decompose water, the hydrates are formed by a secondary action in the aqueous solution. Their formation can be limited by Bunsen's method of using a powerful current and a small cathode, so that more metal is deposited than can be decomposed by the water present.

[1] The notion that chloride and bromide of iodine are electrolytes proceeded from an erroneous view of the nature of their aqueous solutions.

[2] Bleekerode, *Wied. Ann.* 1878, iii. 166; for HF and HCl *vide* also Gore, *Roy. Soc. Proc.* 1869, 256.

[3] F. Kohlrausch, *Göttingen. Nachr.* April 4, 1877, 196.

[4] *Pogg. Ann.* 1874, Jubelband, 135.

[5] For most of these elements only the chlorides have been examined. It is only in a few cases that the bromides, fluorides, and iodides have been investigated.

[6] Buff, *Liebig's Annalen*, 1859, cx. 273; Hittorf, *Pogg. Ann.* 1859, cvi. 390

[7] Hillebrand and Norton, *Pogg. Ann.* 1875, clv. 633; clvi. 466; clviii. 71.

[8] The elements in brackets have not been investigated.

The heavy metals of the first three families resemble the preceding groups on the whole.

I. B : Cu, Ag, Au,
II. B : Zn, Cd, Hg,
III. B : Ga, [In], [Tl].

As far as they have been investigated, they are analogous to the preceding groups, but still some points of difference do exist.

Molten cuprous chloride[1] and silver chloride decompose thus :—

$$Cu \mid Cl \text{ and } Ag \mid Cl, \text{ or } Cu_2 \mid Cl_2 \text{ and } Ag_2 \mid Cl_2.$$

The analogous chloride of gold, AuCl or Au_2Cl_2, and auric chloride, $AuCl_3$, are not fusible, and consequently have not been investigated.

Anhydrous cupric chloride, $CuCl_2$, loses half its chlorine on fusion, and cannot therefore be examined. The aqueous solution decomposes in the same way as all the other cupric salts, thus, $Cu \mid Cl_2$.

If the same current were passed through molten cuprous chloride and a solution of the cupric chloride, the same quantity of chlorine would be liberated from both the salts, but the cuprous salt would deposit twice as much copper as the cupric, $Cu_2 \mid Cl_2$, and $Cu \mid Cl_2$, in the same time that H_2 or Ag_2 is liberated in the voltameter. Copper is electrolytically mono- and di-valent.

Whether the decomposition of an aqueous solution of gold chloride is analogous, $Au \mid Cl_3$, and whether the metal is electrolytically trivalent has not yet been decided,[2] as the solution cannot be obtained free from hydrochloric acid. In the acid solution, and in that of the double salts, $KCl . AuCl_3$, &c., gold is reduced by a secondary reaction. According to Kohlrausch[3] silver iodide, AgI, differs from the bromide and chloride because its conductivity diminishes when it is cooled below its melting point (540°) at about the same rate that it does in the molten state. It is only at 145°, when the substance becomes crystalline, that the conductivity rapidly diminishes.

[1] H. Buff, *Liebig's Annalen*, 1859, cx. 269.
[2] Hittorf, *Pogg. Ann.* cvi. 391.
[3] *Wied. Ann.* 1882, xvii. 642.

$ZnCl_2$ and $CdCl_2$ are good electrolytes in the molten state[1] or in solution. The corresponding chloride of mercury, $HgCl_2$, is an exceedingly bad conductor[2] in the fused state or in a perfectly neutral solution. The solution soon becomes acid, and is then a better conductor. The mercury, deposited in the ratio of one equivalent Hg to H_2, is partly if not entirely due to a secondary action of the hydrogen. It is still questionable whether $HgCl_2$ is an electrolyte. The solid mercuric iodide HgI_2 begins to conduct below its melting-point, so soon as it is changed to the yellow modification by heat. Faraday considered it to be a conductor of the first class, but Beetz[3] has proved that it undergoes decomposition to a certain extent. The mercury in calomel, HgCl or Hg_2Cl_2, is probably monovalent, like Cu and Ag in their insoluble chlorides.

Buff[4] obtained the equivalent of Hg for one equivalent of H from the basic mercurous nitrate. The compounds of the rare heavy metals of the family III. B: Ga, In, Tl, have not been examined in the molten state. Tl is probably monovalent in thallous chloride. $TlCl_3$ decomposes on fusion. Gallium is deposited from its solution on electrolysis, and this will doubtless be the case with indium and thallium.

§ 289. The elements of the four remaining groups, and also boron, exhibit a considerable difference in their behaviour from those of the first three groups.

According to Faraday, BCl_3 by itself is a non-conductor; so also are the chlorides of family IV. A: C, Si, Ti, Zr, (Th ?). CCl_4 and $SiCl_4$, which were examined by Faraday; $TiCl_4$ and $ZrCl_4$, according to Becquerel,[5] are non-conductors. The electrolysis of titanium and zirconium chlorides containing iron (observed by Becquerel) is probably due to a secondary action. Thorium chloride has not been investigated. In the second group of this family, which embraces the easily reducible metals,

IV. B: Sn, Pb,

[1] According to F. Braun (*Wied. Ann.* 1882, xvii. 625) perfectly anhydrous $ZnBr_2$ and ZnI_2 are not electrolytes.

[2] Buff, *Liebig's Annalen*, cx. 271. [3] *Pogg. Ann.* 1854, xcii. 457.

[4] *Loc. cit.* 270. [5] *Ann. Chim. Phys.* [2] 1831, xlviii. 348.

Buff[1] has investigated stannic chloride, $SnCl_4$, and found that it is a non-conductor in the anhydrous state. The aqueous solution is decomposed into tin and chlorine, but Hittorf[2] has shown that this is due to a secondary action. The hydrochloric acid formed by the action of water on the chloride is electrolysed, and the hydrogen reduces the tin.

§ 290. On the other hand the chlorides of the type RCl_2, or more correctly R_2Cl_4, viz. Pb_2Cl_4, and Sn_2Cl_4, are electrolytes in the molten state and in solution. In these compounds the metals are divalent, Sn and Pb being equivalent to H_2. According to Faraday lead fluoride, Pb_2Fl_4, is a conductor of the first class, but Beetz[3] has proved that this compound is also an electrolyte.

In the fifth family, V. A : V, Nb, Ta,
V. B : N, P, As, Sb, Bi,

the chlorides of group A, and also $BiCl_3$ have not been examined. But as PCl_3, $AsCl_3$, $SbCl_3$, and $POCl_3$ in the isolated state are non-conductors, this is probably true of the whole family V.

The aqueous solution of the chlorides of V. B are, like those of stannic chloride, decomposed by the secondary action. The metals are reduced by the H resulting from the electrolysis of the hydrochloric acid. A hydrochloric acid solution of $SbCl_3$ yields explosive antimony.[4]

The halogen compounds of the group VI. B : O, S, Se, Te are, as far as they have been examined, non-conductors. So also are the compounds which the halogens VII. B : Fl, Cl, Br, I, form with each other, *e.g.* iodine chloride or bromide.

The aqueous solutions of the latter are decomposed by electrolysis because they contain iodic and hydrochloric or hydrobromic acids.

The chlorides, bromides, and oxychlorides of the following amilies are electrolytes.

VI. A : Cr, Mo, W, U.
VII. A : Mn
VIII. *a* : Fe, Co, Ni.

[1] *Ann. Chim. Phys.* [2] 1831, xlviii. 273.
[2] *Pogg. Ann.* 1859, cvi. 396. [3] *Ibid.* 1844, xcii. 460.
[4] Gore, 1858, *Phil. Trans.* loc. cit. ; *Jahresbericht Chem.* 1858, 177, 179 ; Pfeiffer, *Liebig's Annalen*, 1881, ccix. 161.

The analogous compounds of

VIII. *b* : Ru, Rh, Pd, and VIII. *c* : Os, Ir, Pt,

are probably also electrolytes.

Bunsen[1] has proved this for Cr_2Cl_6 and Mn_2Cl_4, and Hittorf[2] has demonstrated the same for UO_2Cl_2 and Fe_2Cl_6, and Buff[3] has also shown the probability of Fe_2Cl_6 being an electrolyte. The anhydrous uranium oxychloride was experimented on in the molten state, and the other chlorides in aqueous solution. The decomposition of these solutions was not due to a secondary reaction, as the metals are only obtained with currents of great density, *i.e.* with very small cathodes. If a large cathode is used the metal distributed over its surface remains in contact with the solution and decomposes water. Hittorf has also proved that the metal is really transported by the current, and not, as is the case with tin, reduced at the place it happens to be in. In the case of Cr_2Cl_6 and Fe_2Cl_6 it is undecided whether the chlorides are at once split up into metal and chlorine, $Cr_2 \mid Cl_6$ and $Fe_2 \mid Cl_6$, or whether they are first reduced to the lower chlorides and then decomposed,

$$Cr_2 \mid Cl_4 \text{ and } Fe_2 \mid Cl_4.$$

In either case three atoms of chlorine appear at the anode for one atom of metal at the cathode. The changes are either

$$Fe_2Cl_6 = Fe_2 + 3Cl_2,$$

or $$Fe_2Cl_6 + 2HCl = Fe_2Cl_6 + H_2 + Cl_2$$

$$= Fe_2Cl_4 + 2HCl + Cl_2 = Fe_2 + 2HCl + 3Cl_2,$$

so that the results are the same in either case. The formation of the lower chlorides precedes the precipitation of the metals, but we do not know whether the reduction is brought about by hydrogen or by the liberated metal.

§ 291. The results of the investigations mentioned in the preceding sections may be summarised as follows:—The chlorides of families I., II., III., VI.A, VII.A, and VIII., are with few exceptions electrolytes. The chlorides of groups IV.A, V.A (?) and B, VI.B and VII.B, are non-conductors. What is

[1] *Pogg. Ann.* 1854, xci. 619. [2] *Pogg. Ann.* 1859, cvi. 386 and 390.
[3] *Liebig's Annalen*, 1859, cx. 274; xciv. 22.

the cause of this difference? Is it due to the fact that the compounds capable of undergoing electrolytic decomposition contain elements which are electropositive, and are conductors of the first class, and that the chlorides which are non-conductors chiefly contain negative elements which are non-conductors? or is it due to the fact that the non-conducting compounds cannot be heated to redness on account of their volatility, and cannot therefore be examined in that condition which Kohlrausch[1] declares to be a *sine quâ non* for the electrolysis of an unmixed body. The first hypothesis is not generally applicable, as we not only have the following non-conductors, B, C (as diamond), Si, Ti, Zr, P, S, Cl, Br, I, amongst the constituents of the non-conducting chlorides, but also the following conductors of the first class C (as graphite), and Sn, As, Sb, Sr, Te.

The second hypothesis meets with few exceptions. All chlorides and analogous compounds known as non-conductors are easily volatile, and on this account have not been examined at a red heat,[2] whilst those chlorides which are electrolytes are bodies melting at a high temperature.

Hence it appears that the decomposability of the pure unmixed chlorides by electricity depends on the nature of their constituents in so far as these determine their fusibility and volatility, as only those compounds can undergo electrolysis which can remain in the molten state at high temperatures.

Even this view cannot be absolutely correct, although it is confirmed by the behaviour of the chlorides in group IIB. The difficultly volatile $ZnCl_2$ and $CdCl_2$ are electrolytes, the readily volatile $HgCl_2$ is a non-conductor. Of the chlorides of tin the volatile $SnCl_4$ is a non-conductor, the less volatile $SnCl_2$ is an electrolyte. We must remember that those compounds which are non-conductors when isolated, are only decomposed by a secondary action in aqueous solution, and consequently differ essentially from the true electrolytes, in their behaviour under precisely similar conditions. It

[1] § 286, p. 567, *loc. cit.*

[2] It would be interesting to learn whether any of these bodies would become conductors if they were heated in closed vessels almost to their critical temperatures.

appears doubtful whether the non-conducting chlorides which are liquid at low temperatures would be changed to electrolytes at a red heat. This is a problem which would be very difficult to solve, but its experimental solution is much to be desired.

§ 292. Generally speaking, the oxides and sulphides are analogous to the chlorides in their behaviour. There is this difference, that some oxides and sulphides are conductors of the first class, and this is very rarely, if ever, the case with chlorides. All those oxides and sulphides are non-conductors which are liquid at low temperatures, and are easily volatile. Bleekerode[1] states that the following compounds are non-conductors, H_2O, H_2S, CO_2, CS_2, NO_2, SO_2, SO_3, OsO_4, and that the anhydrides of arsenious and boric acids, As_2O_3 or As_4O_6, and Bo_2O_3, which melt at high temperatures, are also non-conductors.

The anhydrides V_2O_5, CrO_3 and MoO_3 are electrolytes according to Buff[2] and Bleekerode, but Hittorf[3] states that molten CrO_3 and CrO_2Cl_2 are non-conductors. Most of the oxides which require a high temperature for fusion are non-conductors in the solid and electrolytes in the molten state. But many oxides, such as PbO, SnO_2, Cr_2O_3, Fe_2O_3, Fe_3O_4, MnO_2 are conductors in the solid state, although they differ from true conductors of the first class, by their conductivity, like that of all electrolytes, increasing instead of diminishing with a rise of temperature.[4]

If they really do conduct without decomposition, these oxides occupy a position between the two classes of conductors.

The oxides of two elements, and especially the salts of their oxyacids, are almost without exception electrolytes both molten and in solution. Their behaviour is analogous to that of most of the salts of the halogen acids. Many of the acids which are liquid at the ordinary temperature, *e.g.* sulphuric acid H_2SO_4,[5] nitric acid HNO_3,[6] are in the isolated anhydrous

[1] *Wied. Ann.* 1872, iii. 166, 171. As regards SO_3, this had been previously proved by Magnus, *Pogg. Ann.* 1858, civ. 579, and Geuther, *Liebig's Annalen*, 1859, cix. 130.

[2] *Lieb. Ann.* cx. 275. [3] *Pogg. Ann.* 1859, cvi. 567. [4] Buff. *loc. cit.* 288.

[5] *Wiedemann's Galvanismus*, 2nd edition, i. 326.

[6] F. Kohlrausch, *Wiedemann's Ann.* 1879, vi. 165.

state, non-conductors, or much worse conductors than their aqueous solutions, which are without exception good conductors.

It is remarkable that many salts are good electrolytes whose constituents are either poor or non-conductors, *e.g.* the salts which ammonia forms with carbonic, acetic, and hydrocyanic acids.[1]

As the salts of ammonium closely resemble the salts of the alkalis in their conductivity, and as the solution of ammonia is distinguished from the alkaline hydrates by its feeble conductivity, Kohlrausch rightly concludes that the aqueous solution of ammonia contains very little or no ammonium hydrate NH_4OH, the presence of which is erroneously maintained in many modern text-books.

§ 293. More conductors of the first class are found amongst the sulphides than amongst the oxides, but many of them are no doubt electrolytes. A careful research of Hittorf[2] has shown that it is very difficult to discriminate between the two classes. Not only in the experiment, but also in the interpretation of its results, many difficulties are met with.

Most sulphides of the heavy metals are conductors of the first class according to Hittorf, *e.g.* CuS, Hg_2S, HgS, SnS_2, Bi_2S_3, FeS, FeS_2 CoS, NiS.

On the other hand, Cu_2S and Ag_2S are electrolytes; their resistance diminishes with the temperature. Probably the following sulphides ZnS, CdS, SnS, MnS, Sb_2S_3,[2], which are non-conductors at low temperatures, behave in a similar manner.

Hittorf calls attention to the fact that most, if not all, the metallic sulphides which are deposited from their solutions as black precipitates, are conductors of the first class, but the coloured precipitates are non-conductors; *e.g.* red cinnabar is a non-conductor, but black sulphide of mercury, HgS, is a conductor of the first class.

Only the sulphides of the alkalis and alkaline earths can be examined in solution, as the other sulphides are either insoluble or are decomposed by water. The sulphides of the alkalies are excellent electrolytes;[3] they stand in the same

[1] Kohlrausch, *loc cit.* 190–191.

[2] The formula is not given, but Sb_2S_3 must be meant, as Sb_2S_5 loses sulphur on fusion.

[3] From a private communication of Kohlrausch's.

relation to sulphuretted hydrogen that the alkalis do to the non-conductor water.

A further investigation of the electrochemical behaviour of all the sulphides is very desirable, because this class of compounds forms the connecting link between the conductors of the first class and electrolytes. If it is possible for one and the same body to be a 'metallic' conductor, and an electrolyte, or non-conductor, examples will be found amongst the sulphides. In nature, abrupt transitions without connecting links are rare. The remarkable results of Hittorf's investigation, which prove that in the electrolysis of cuprous and silver sulphides a 'metallic' conductivity is soon established, will probably have an important bearing on our knowledge of both kinds of conductivity. In the case of cuprous sulphide threads of metallic copper and also of cupric sulphide are produced, both of which are 'metallic' conductors.

Whether the sulphides which are conductors of the first class resemble all other conductors as regards the decrease in their conductivity with an increase in temperature does not appear to have been investigated.

Hittorf[1] has shown that the resistance of cuprous selenide and silver selenide, Cu_2Se and Ag_2Se, increases with the temperature. They are therefore conductors of the first class, and differ in this respect from the analogous sulphides. Probably the remaining metallic selenides belong to this class, although Hittorf[2] and W. Siemens[3] have shown that the conductivity of amorphous selenium increases with the temperature, but the conductivity of crystalline selenium diminishes with the temperature. One modification of selenium is an electrolyte, the other a metallic conductor. This can only be explained on the supposition that the movement of the electricity in this element is of two kinds, one kind of movement is facilitated by the increased motion of the particles by heat, and the other is retarded. This may also hold good for the metallic sulphides and selenides.

Sulphur and selenium stand on the border line which

[1] *Pogg. Ann.* 1851, lxxxiv. 28. [2] *Ibid.* 217.
[3] *Ibid.* 1876, clix. 119.

separates the negative elements capable of acting as anions from the rest. If the most negative families are arranged in the same order as in the table § 61, p. 120, then the elements capable of acting as anions are found on the right of the line

C	N	O	F
Si	P	S	Cl
	As	Se	Br
	Sb	Te	I

Those conductors of the first class which are composed of elements on the left of this dividing line with more positive elements should be more carefully examined, more especially with a view of ascertaining whether all metallic nitrides, phosphides, arsenides, selenides, and tellurides possess a conductivity which decreases with an increase in temperature. This has been shown to be the case for all alloys of the positive metals and also for copper arsenide.[1]

§ 294. The two kinds of electrical conductivity differ essentially from each other. In metallic conductors the electricity is passed on from one particle to another, but there is no change in the position of the particles themselves. In electrolytes the particles move with the electricity, but the passage of the electricity from one particle to another is not excluded. This doubtless frequently happens, but the electricity cannot change its place without some particle moving with it. It always requires a carrier, which it may change as a rider changes his horse. These carriers of electricity are not whole particles or molecules, but fractions of molecules. Some flow with, others against the current; the former are charged with a definite amount of positive, and the latter with a definite quantity of negative electricity.

It is very remarkable, and at first sight very puzzling, that these molecular fractions, the *ions*, which were originally combined together, only appear at points far apart, viz. the surfaces of the electrodes. Not the slightest trace of them can be detected in the mass of the electrolyte lying between these points.

[1] Wiedemann, *Galvanismus*, 2nd edition, i. 305.

Many theories have been promulgated to explain this remarkable phenomenon. The oldest, that of Grotthuss,[1] is no longer tenable, as it regards the electrolytes as a regularly arranged aggregation of molecules in a state of rest, but we are now compelled to consider that in every liquid, and consequently in every electrolyte, there is an active and irregular movement of the isolated particles. Although the particles are isolated, they adhere to each other with a certain amount of cohesion. A closer examination of the phenomenon of electrolysis also shows that the movement of the ions does not take place with that amount of regularity Grotthuss supposed.

Although the nature of electrolysis is not clearly understood at the present time, there is no doubt that the passage of the electricity through the electrolytes is intimately associated with the different movements which occur in liquids in the absence of electrical excitement. These movements are rather used in the passage of the electricity than caused by it.

The electrolysis of a homogeneous molten substance, which appears to be the simplest case, is difficult of observation, because in this case it is only the appearance of the ions at the electrodes and any secondary effects they produce which are perceptible. No change can be observed in the circuit itself, in the mass of the electrolyte. The changes in an electrolytic mixture of several bodies are more easy to study. In an aqueous or alcoholic solution conclusions may be deduced from the changes in composition of the electrolyte in different parts of the circuit. Our present knowledge of electrolysis has been chiefly derived from the investigation of aqueous solutions.

§ 295. The separation of the ions at the electrodes first proceeds from that portion of the electrolyte which is in direct contact with the electrodes. But this loss is partly made good by the mass lying between the electrodes, so that finally, after the current has been maintained for a sufficient length of time, the anions are found at the anode, and the cations at the cathode. This movement is termed a *migration of the ions* by

[1] *Vide* Wiedemann, *Galvanismus*, 2nd edition, i. 614.

Hittorf,[1] whose investigations have thrown much light on these phenomena. He confirmed by numerous careful experiments the predictions of L. Gmelin, Daniell and Miller, that the two ions do not migrate at the same rate. He determined quantitatively the relative rate of migration of a very large number of ions, and corrected by these determinations many persistent, long-standing errors concerning their nature and composition, showing that many substances regarded as cations are deposited by a secondary action, and that they really move towards the anode.

By means of ingenious but simple apparatus, the experiment was modified so as to leave the middle layer of electrolyte unaltered in composition, because up to the time when the electrolysis ceased, this middle layer did not part with more than it was receiving from the adjacent layers. In this way he obtained 'migration values,' *i.e.* the relation between the equivalents of the ions which have passed through this unaltered section, and the quantities of the equivalents deposited at the electrodes.

From a solution of 1 part of copper sulphate crystals $CuSO_4\ 5H_2O$, in 5·75 parts of water, 0·2955 gramme of Cu were deposited on the cathode, but only 0·0843 gramme Cu passed through the unaltered layer, or, to 1 equivalent of precipitated Cu,

$$\frac{843}{2955} = 0{\cdot}285 \text{ equivalent Cu.}$$

As the precipitated copper was combined with 1 equivalent of SO_4, and as the solution at the cathode only contained neutral salt and water after electrolysis, $1 - 0{\cdot}285 = 0{\cdot}715$ Eq SO_4 must have migrated through the unaltered section to the anode. If both the ions moved at the same rate, half an equivalent of each ion would pass through the middle layer; for under this assumption each half of the solution sends equal quantities of the ions to the electrodes. The liquid at the cathode would deposit 0·5 Eq Cu, and transmit 0·5 Eq SO_4 through the middle layer to the anode; the solution at the

[1] 'De Iontum Migrationibus Electrolyticis,' *Habilitationsschrift*, Münster, 1853; *Pogg. Ann.* 1853, lxxxix. 177; 1856, xcviii. 1; 1858, ciii. 1; 1859, cvi. 337, 513.

anode would send 0·5 Eq Cu through the central section to the cathode, and 0·5 Eq SO_4 direct to the anode. But as 2·5 SO_4 to 1 of Cu pass through the unaltered layer, it is evident that in this instance the anion SO_4 migrates much more rapidly than the cation Cu. The layer which maintains its composition unaltered the longest does not lie in the middle between the electrodes, but is much nearer the cathode.

In most of the examples examined by Hittorf, the anion moves much more rapidly than the cation, especially in the electrolysis of the salts of most of the strong mineral acids. But in the acetates and cyanides the reverse takes place, the cation moves more rapidly. The metals of the alkalis, especially potassium, migrate only a little, if at all, slower than chlorine, bromine, iodine, and other anions, but both the light and heavy diad metals move much more slowly.

As a rule, the rate of migration of the negative constituent, the anion, increases with the concentration of the solution, but the reverse is true of many salts of the alkalis, *e.g.* potassium nitrate, chlorate, and cyanide, sodium nitrate and acetate. Hydrochloric acid diluted with 82 times its weight of water exhibits its minimal rate of migration for Chlorine. Sulphuric acid diluted with 5 parts by weight of water is in a similar position as regards SO_4; additional dilution or concentration increases the rate.

§ 296. Not only the ions, but the solvents also move. Water always moves in the direction of the positive current, and so also do some other non-conducting liquids, alcohol, turpentine, and carbon bisulphide, as a general rule, but under certain conditions they move in the opposite direction. This movement of the solvent is not, as a rule, perceptible, because it causes an inequality of the hydrostatic pressure in the liquid, which at once corrects itself. It can only be observed when this compensatory movement is hindered. It was discovered in 1807 by Reuss,[1] in Moscow, who separated the liquid in two parts by means of a porous partition, which interfered with the movement of the return current. This phenomenon he termed 'motus stöchiagogus.' Porret, Becquerel, Wiedemann, Hittorf, Quincke and other physicists

[1] *Vide* Wiedemann, *Galvanismus*, 2nd edition, i. 576.

have investigated the phenomenon, which is generally known as 'electric endosmose.' A more suitable appellation is that proposed by E. du Bois Reymond, viz. 'the cataphoric action of the current.' The movement may be observed in any case where the path of the current is considerably contracted by non-conducting solid bodies, in glass capillaries, or in porous partitions composed of earthenware plates, or of sand, clay, sulphur, charcoal, &c. Solid particles suspended in water are carried along by the current.

According to Hittorf's experiments [1] the movement of the solvent has no influence on the rate of migration. Hence it follows that both are carried along in the same way by the water. The solution moves as a whole, for if the motion of one of the ions is more strongly influenced than that of the other, the rate of migration of the cation will be increased in each case. Although the motion of the ions and that of the whole solution are independent of each other, still, they bear the same relation to each other under similar external conditions, as they are both proportional to the strength of the current.

Quincke [2] has observed that just as the electric current forces a liquid through a porous wall, in the same way, when a liquid is forced through a porous partition, it produces a stream of electricity, flowing in the same direction. This observation throws much light on the intimate relation between the motion of the liquid and the forces exciting the electric current.

The production of a current by the contact of a metal with two solutions of different degrees of concentration of one of its own salts, probably depends on the same cause. This phenomenon was predicted by Helmholtz [3] on theoretical grounds, and was discovered experimentally by James Moser.[4] If two vessels, filled with solutions of zinc sulphate of different degrees of concentration, are connected by a syphon, then, by immersing two similar zinc plates in metallic contact with each other, one in each vessel, an electric current will flow from the dilute to the strong solution and return through the metal. The current flows in the same direction as the diffu-

[1] *Pogg. Ann.* 1856, xcviii. 8.
[2] *Ibid.* 1859, cvii. 1; 1860, cx. 38.
[3] *Wied. Ann.* 1878, iii. 201.
[4] *Ibid.* 1878, iii. 216.

sion of the water. Zinc is precipitated at the cathode, and the same quantity of zinc is dissolved from the anode. The total thermic effects of the chemical action in this element are therefore null. The force required for the movement of the electricity is derived from the diffusion. These experiments justify the assumption that the flow of electricity is always accompanied by a current of water; the latter is not observed because the liquid generally flows back to its original level. It is by no means improbable that the mass of a molten electrolyte moves, as well as the ions, but at present this has not been ascertained. The electrolysis of a solution is rather a complicated process; the solutions move as a whole, and the two ions move in opposite directions.

§ 297. As the movement of the electricity is connected with that of the ions, it has to overcome any obstacles which oppose a change in the position of the ions. The conductivity of an electrolyte increases with the mobility of the particles which it yields on electrolysis, or the resistance increases with their want of mobility. Since electrolysis consists in the motion of both the ions, the conductivity depends on the nature of the two ions. It is determined by the sum of their mean velocities. This is proved by the observations of F. Kohlrausch,[1] who has systematically and exhaustively investigated the relation between the conductivity of a body and its chemical composition. With the aid of Hittorf's determinations of the rate of migration,[2] he has been able to calculate the velocities of the individual ions in a large number of electrolytes from their observed conductivity.

In dilute solutions the constants of conductivity c are very nearly proportional to the concentration, *i.e.* to the number m of electrolytic equivalents contained in the unit of volume.

$$c = m \cdot \lambda.$$

When the factor λ represents Kohlrausch's 'specific molecular conductivity,' $\lambda = u + v$. The specific molecular conductivity is the sum of the values u and v, which are proportional to the individual velocities of the ions. Their

[1] *Wied. Ann.* 1879, vi. 1, 146. [2] *Loc. cit.* 295.

relation to Hittorf's rate of migration n is expressed by the equation

$$u : v = 1 - n : n ;$$

from which it follows that

$$n = \frac{v}{u + v}, \quad 1 - n = \frac{u}{u + v}.$$

As n, c and m can be determined by experiment, the velocities of all the ions can be measured by the same standard of comparison,

$$u = (1 - n)\frac{c}{m} = (1 - n)\lambda, \quad v = n\frac{c}{m} = n\lambda,$$

and may all be expressed in terms of absolute measurement.

By means of this formula Kohlrausch calculated the mobility of the ions for fluorides, chlorides, bromides, iodides, cyanides, hydrates, chlorates, nitrates, and acetates of the alkali metals, including ammonium, also of hydrogen, silver, the metals of the alkaline earths, and of some of the heavy metals. He obtained closely concordant results for the mobility of the ions from observations made with perfectly distinct bodies. The mean values expressed in Kohlrausch's unit are given in the following table:—

Cations	$u \cdot 10^7$	Cations	$u \cdot 10^7$	Anions	$v \cdot 10^7$	Anions	$v \cdot 10^7$
H	278	$\frac{1}{2}$Mg	23	OH	141 [1]	NO_3	46
Li	21 [1]	$\frac{1}{2}$Ca	26	F	30	ClO_3	40
Na	31 [1]	$\frac{1}{2}$Sr	28	Cl	49 [1]	$C_2H_3O_2$	23
K	48 [1]	$\frac{1}{2}$Ba	29	Br	53		
NH_4	47	$\frac{1}{2}$Cu	29	I	53 [1]		
Ag	40	$\frac{1}{2}$Zn	20	CN	50		

If the conductivities and rates of migration are recalculated from these numbers they will be found in most cases to agree closely with the experimental results. The velocities clearly depend on the atomic weights. In all the families examined they increase with the atomic weights.

Li Na K $\longrightarrow$ Mg Ca Sr Ba $\longrightarrow$ F Cl Br I $\longrightarrow$

The alkali metals have a greater mobility than the equivalent quantities of the metals of the alkaline earths, and the

[1] These numbers have been confirmed by J. Kuschel (*Wied. Ann.* 1881, xiii. 289).

heavy metals, Cu, Ag, belonging to the same group, move more rapidly than Zn, which is associated with the group of alkaline earths. Ammonium has nearly the same mobility as potassium, with which it is isomorphous. Experiments made with the salts of dibasic acids (sulphuric and oxalic) gave very different results, but at present these exceptions cannot be explained. The following numbers were obtained for sulphuric acid and its salts.

	$\lambda 10^7$	n	$u 10^7$	for	$v 10^7$	for
$\frac{1}{2}H_2SO_4$	206	0·20	164·8	$\frac{1}{2}H_2$	41·2	$\frac{1}{2}SO_4$
$\frac{1}{2}Na_2SO_4$	63	0·63	23·3	$\frac{1}{2}Na_2$	39·7	,,
$\frac{1}{2}K_2SO_4$	79	0·50	39·5	$\frac{1}{2}K_2$	39·5	,,
$\frac{1}{2}MgSO_4$	37	0·63	13·7	$\frac{1}{2}Mg$	20·9	,,
$\frac{1}{2}CuSO_4$	33	0·64	11·9	$\frac{1}{2}Cu$	21·1	,,
$\frac{1}{2}ZnSO_4$	34	0·64	12·2	$\frac{1}{2}Zn$	21·8	,,

Here the mobility of hydrogen and of the metals is much smaller than it is in the electrolysis of the salts of monobasic acids, viz. in the proportion of

40 : 48 = 1 : 1·20 for K
23 : 31 = 1 : 1·35 ,, Na
14 : 23 = 1 : 1·64 ,, $\frac{1}{2}$Mg
12 : 20 = 1 : 1·67 ,, $\frac{1}{2}$Zn
165 : 278 = 1 : 1·68 ,, H
12 : 29 = 1 : 2·15 ,, $\frac{1}{2}$Cu

These results show that the mobility of each of these cations diminishes as it becomes less positive. What law governs this relation is not at present known.

Kuschel [1] has shown that in the carbonates, the alkali metals with the exception of lithium have the same mobility as in the salts of monobasic acids, $CO_3 = 29$.

According to Kohlrausch the difference in the mobility of the monovalent metals may be explained on the supposition that the metals are deposited as single atoms, *e.g.* Kx, from compounds with monovalent anions, but on the electrolysis of the sulphates they are liberated as double atoms, K_2x, which move more slowly than the single ones. But there is no difference in the mobility of anions such as Cl, whether they are liberated from monovalent or divalent metals. But the anion SO_4 moves twice as fast when the cation is monovalent as

[1] *Wied. Ann.* 1881, xiii. 297.

when it is divalent. Kohlrausch [1] points out that there are many other grounds for believing that there is a difference in the constitution of sulphates of mono- and di-valent metals.[2] From the small number of experiments that have been made it appears that the oxalates behave like the sulphates.

§ 298. It must be mentioned that the determination of mobility yields uncertain results where O or H or both appear as ions. It is obvious that the rate of migration of these elements of water cannot be determined in aqueous solution, so that it is not known with certainty how the electrolyte is decomposed. In consequence of this, opinions are divided on the electrolysis of sulphuric acid, the alkaline hydroxides, and other hydrogen compounds.

Assuming that sulphuric acid is decomposed according to the equation

$$H_2 \mid SO_4 = H_2 \mid SO_3O,$$

then the rate of migration n for the anion $SO_4 = 0{\cdot}20$.

But under the equally probable supposition that the electrolysis takes place thus,

$$H \mid HSO_4,\ H_4 \mid SO_5 \text{ or } H_6 \mid SO_6 \text{ (Bourgoin)},$$

then $n = 0{\cdot}10$, $n = 0{\cdot}40$ or $n = 0{\cdot}60$.

For in the first of these three cases, each SO_3 is equivalent to H, not H_2, in the second case it is equivalent to H_4 in the third to H_6.

But as λ varies with the electrolytic equivalent of the compound, the anion will have the same velocity, but that of hydrogen will vary to a considerable extent, viz, :

	$\lambda\ 10^7$	n	$u\ 10^7$	for	$v\ 10^7$	for
H, HSO_4	412	0·10	370·8	H	41·2	SO_4H
$\frac{1}{2}H_2, SO_4$	206	0·2	164·8	$\frac{1}{2}H_2$	41·2	$\frac{1}{2}SO_4$
$\frac{1}{4}H_4, SO_5$	103	0·4	61·8	$\frac{1}{4}H_4$	41·2	$\frac{1}{4}SO_5$
$\frac{1}{6}H_6, SO_6$	68·7	0·6	27·4	$\frac{1}{6}H_6$	41·2	$\frac{1}{6}SO_6$

Different values are also obtained for H and O according as we assume that the electrolysis of the alkali hydroxides takes place according to the equation

$$K \mid OH \text{ or } KH \mid O,$$

[1] *Wied. Ann.* 1881, xiii. 179.

[2] *Vide* § 179.

and that of dilute hydrogen acids as

$$H \mid Cl \text{ or } H_3\,Cl \mid O.$$

The former formula for the alkali hydroxides has the preference, as Kuschel has shown that when a mercurial cathode is used, the metal is dissolved and no hydrogen evolved.

§ 299. There is another source of uncertainty in determining the mobility of certain metals, as Hittorf[1] has observed that in the concentrated solution of their salts the rate of migration of the anion is found to be $n > 1$ or even $n > 2$.

Even if the cation did not move at all, the velocity n would at the most equal 1, *i.e.* the quantity transferred would be equal to the amount deposited on the electrode. But as the latter is greater than the former, and $(1-n)$ is a negative quantity, Hittorf concluded that concentrated solutions of these salts, more especially the chlorides and iodides of cadmium and zinc, do not decompose according to the equation $Cd \mid I_2$ but $Cd \mid Cd\,I_4 = Cd \mid CdI_2, I_2$, or in concentrated alcoholic solutions $Cd \mid Cd_2\,I_6 = Cd \mid 2\,CdI_2, I_2$ analogous to the double salts $K_2 \mid Cd\,I_4 = K_2 \mid CdI_2, I_2$.

He also points out that n grows rapidly smaller with the dilution of the solution, because the water splits up the double molecules into single molecules.

Grotrian[2] has recently determined the conductivity of some other cadmium salts, and with the aid of former determinations has calculated the mobility of Cd, in order to explain the peculiar behaviour of its salts. He obtained very different values if he used the ordinary molecular weights of the salts in his calculations, but he obtained concordant results if he took different multiples to represent the electrolytic quantities.

This peculiar behaviour of the cadmium salts[3] is well worthy of attention, because it shows that the ordinary groups of atoms which act as anions may, under certain conditions, carry other groups with them which do not bring any electricity to the electrode.

In this case, we find anions composed of an active (*i.e.* bearing electricity) and a passive fraction; the question is

[1] *Pogg. Ann.* 1859, cvi. 542. [2] *Wied. Ann.* 1883, xviii. 177.

[3] This in all probability is in some measure related to the irregularities observed in the heats of formation of cadmium salts, mentioned in § 224.

whether this does not frequently occur. The rate of migration of cadmium iodide like that of many other electrolytes varies greatly with the concentration of the solution; for concentrated sulphuric acid the velocity is more than double that of the moderately dilute acid. It is probable that in the former case, one equivalent is electrolysed and another is carried along by it.

$$\overset{+}{H_2} \mid \overset{-}{SO_4}H_2SO_4.$$

Continuing this speculation, it appears doubtful whether SO_4 really is an anion, whether it is not more probable that only the oxygen atom which is set free by the electrolysis is the true anion and that the SO_3 is carried along by it.

$$\overset{+}{H_2} \mid \overset{-}{O}\cdot SO_3$$

This hypothesis would explain the curious fact that in many of the different oxygen acids, *e.g.* the different phosphoric acids, very different quantities appear at the anode for one equivalent of oxygen or one equivalent of negative electricity, according to the extent with which they are saturated by positive metals.

Hittorf[1] investigated the electrolysis of the phosphates:

$$\underset{\text{Metaphosphate.}}{\overset{+}{Na} \mid \overset{-}{PO_3}} \qquad \underset{\text{Pyrophosphate.}}{\overset{+}{Na_4} \mid \overset{-}{P_2O_7}} \qquad \underset{\text{Orthophosphates.}}{\overset{+}{Na} \mid \overset{-}{H_2PO_4} \qquad \overset{+}{Na_2} \mid \overset{-}{HPO_4}}$$

or

$$\begin{array}{l} \overset{+}{Na} \\ Na \end{array} \left| \begin{array}{l} PO_2, \overset{-}{O} \\ PO_3 \end{array} \right. : \overset{+}{Na_4} \left| P_2O_5, \overset{-}{O_2} \right. : \begin{array}{l} \overset{+}{Na} \\ Na \end{array} \left| \begin{array}{l} H_2PO_3, \overset{-}{O} \\ H_2PO_4 \end{array} \right. : \overset{+}{Na_2} \left| HPO_3, \overset{-}{O} \right.$$

In the same way the electrolysis of the yellow and red chromate may be represented:

$$\overset{+}{K_2}\, CrO_3, \overset{-}{O} \qquad\qquad \overset{+}{K_2} \mid Cr_2O_6\, \overset{-}{O}.$$

This view, which resembles the oldest conceptions of electrolysis, is probably correct. The groups of atoms or radicals transported by the anions may be designated (to use a term of Gerhardt's) as copula of the anions. The next problem is to discover which, among the mass of particles moving against the current, is the true carrier of electricity.

[1] *Pogg. Ann.* 1859, cvi. 404.

§ 300. As the cations are generally single metallic atoms, it does not seem likely that they will transport other atoms. Nevertheless we are acquainted with a series of cases in which we may assume that transportation takes place with the cations as well as with the anions. The bases which are liberated in conjunction with hydrogen at the cathodes in the electrolysis of the salts of ammonium, amines and alkaloids may be considered to be transported by the hydrogen.

Such a hypothesis is clearly permissible on account of its simplicity.

If the electrolysis of the hydrochlorides of ammonium, ethylamine and morphine is represented thus,

$$\overset{+}{NH_4} \mid \overset{-}{Cl} \qquad \overset{+}{NH_3C_2H_5} \mid \overset{-}{Cl} \qquad \overset{+}{NC_{17}H_{20}O_2} \mid \overset{-}{Cl},$$

then the groups of atoms which form the cations are widely different in composition. But if we regard the hydrogen only which is set free at the cathode as the carrier of electricity, and consider that it carries along with it the group of atoms combined with the nitrogen, then the electrolysis of the three salts may be regarded from the same standpoint:

$$\overset{+}{H},\ NH_3 \mid \overset{-}{Cl}, \qquad \overset{+}{H},\ NH_2C_2H_5 \mid \overset{-}{Cl} \qquad \overset{+}{H},\ NC_{17}H_{19}O_3 \mid \overset{-}{Cl}.$$

In the same way we may assume that the varying electrolytic equivalent of many metals, *e.g.* Cu, Hg, is only apparent, as it is really caused by transportation.

The electrolysis of the two chlorides of Cu would be represented as

$$\underset{\text{Cupric.}}{\overset{+}{Cu} \mid \overset{-}{Cl_2}} \qquad \underset{\text{Cuprous.}}{\overset{+}{Cu},\ Cu \mid \overset{-}{Cl_2}}.$$

The copper atom which acts as the carrier of electricity, transports a second indifferent atom of Cu with it in the cuprous salt.

Although such speculations are not only permissible, but in many respects desirable, it cannot be denied that they leave an opening for much caprice. If one of the two monovalent Cu atoms is regarded as an indifferent copula, the same assumption may be made as regards silver or the alkali metals. If the

electrolysis of silver chloride takes place according to the equation

$$\overset{+}{\mathrm{Ag}}, \mathrm{Ag} \mid \overset{-}{\mathrm{Cl}_2}$$

this would, to a certain extent, get rid of the strange fact that a monovalent atom can only transport half as much electricity as a divalent atom, although they both have the same capacity for heat. But the electrolysis of the salts of trivalent metals, such as Al and Fe, would require very complicated hypotheses, so that the advantages thus gained would be counterbalanced by many disadvantages. We must, however, bear in mind the possibility, at any rate in many cases, that the ions consist of an active portion carrying electricity and an indifferent portion or copula.

§ 301. If many doubts exist as to the real facts in electrolysis, the nature of the process is still more enveloped in darkness. None of the known theories can offer a thorough explanation. Some of the former views have been proved untenable, and to this extent the ground has been prepared for further advances. The old idea that the decomposition of the electrolytes is caused by the electricity overcoming the affinity was disputed by Hittorf[1] and has been proved by Clausius to be incorrect in his treatise, 'Ueber die Electricitätsleitung in Electrolyten.'[2] According to the old hypothesis the electrolytes could not conduct electricity and suffer decomposition so long as the electric force remained below the strength which is required to counterbalance the affinity. But as soon as the electric force is greater than that of affinity, a considerable decomposition and a powerful current would suddenly set in. This is quite contrary to our experience, which shows that electrolytic conductivity begins with the feeblest electromotive force, and produces a current obeying Ohm's law, if the polarisation of the electrodes is prevented. The old notion is incompatible with the objection which Berzelius brought against Faraday's laws of electrolysis, viz. that the same quantity of electricity is always required for the decom-

[1] *Pogg. Ann.* 1856, xcviii. 15.
[2] *Ibid.* 1857, ci. 338; *Ges. Abh.* 1867, ii. 202.

position of an equivalent of any compound, independent of the force of the affinities to be overcome.

This protest of Berzelius is justifiable in so far as Faraday's discovery is incompatible with the notions of electrical attraction overcoming affinity; but this does not prove, as Berzelius maintains, that Faraday's law is incorrect; on the other hand it shows that Berzelius's notions of the reaction are untenable, and it proves the necessity of assuming that it is the movement of the ions in a definite direction, not their separation, which is the work of electricity. The decomposition is produced by a different cause.

§ 302. According to Clausius, the separation of the ions is due to the active movements of the particles, molecules as well as atoms, which tend to bring about the dissociation of the compound, so that only bodies capable of dissociation can act as electrolytes. For the purposes of electrolysis it is not necessary that this dissociation should proceed as far as the complete separation and isolation of the constituents, but it is sufficient that there should be a frequent exchange of their constituents when two particles collide, so that each constituent can for a very short time move apart from the other before it again finds an opportunity of uniting with another isolated particle. This sporadic occurrence of isolated molecular fractions is not perceptible to our senses, so long as they are uniformly distributed throughout the whole mass of the electrolyte, but it is only perceptible when some external action collects large quantities of one class of particles at one place and of the others at another.

These views of Clausius are in unison with those which Williamson[1] had previously propounded with regard to the condition of mixed liquids in explaining the process of etherification and other chemical reactions. They form the bases of the kinetic theory of chemical changes, which is now universally adopted. This concurrence in the views of the two investigators is a strong proof of their truth, as they were arrived at from totally different points of view, in attempting to explain two different classes of phenomena, which at first sight do not appear to have the slightest connection with one another.

[1] Liebig's *Annalen*, 1851, lxxvii. 37; Clausius, *Ges. Abh.* 1867, ii. 214.

§ 303. In order to explain electrolysis it is now necessary to assume that as each molecule decomposes, one portion of it carries off a definite, fixed amount of positive electricity, and the other an equivalent quantity of negative electricity. The electricity is either attached to each particle before the separation, or else it is produced at the moment of decomposition. Neither the electric charge nor the decomposition can be observed so long as the same number of particles charged with positive and with negative electricity are found at each part of the electrolyte. This hypothesis is necessary in order that we may understand the fact that a definite quantity of electricity moves with each equivalent of the ions. Clausius considers that the movement of the ions with their accompanying electricity in opposite directions is due to the free electricity, which, according to Kirchhoff, is present at the surface but not in the interior of the circuit. Its action, as far as it can be calculated, is in accordance with Ohm's law,[1] equal in all points of one and the same section perpendicular to the direction of the currents. According to this view electric conduction in electrolytes differs from that in metallic conductors, because in the latter case the electricity passes from particle to particle without any change in the position of the particles, but in electrolytes the ions or molecular fractions accompany the movement of the electricity.[2]

But at the electrodes where one kind of conductivity is transformed into the other, the electricity leaves the ions which are deposited, or, in other words, the ions receive from the electrodes an equal quantity of the opposite kind of electricity, so that they are no longer electrified. Figuratively speaking, the electricities are transported from the electrodes to the contiguous ions (which may be compared to a fleet of ships all of the same tonnage) and are conveyed across the sea of the electrolyte. We must not, however, think that the movement begins at the electrodes, but we must consider that the sea is covered with ships of both kinds of freight, all of

[1] *Vide* Clausius, *Pogg. Ann.* 1858, ciii. 525; Hittorf's reply, *ibid.* 1858, ciii. 53, and 1859, cvi. 583.

[2] It has already been mentioned in § 293 that metallic sulphides in all probability exhibit both kinds of conductivity.

which are moving at the same time, some in this, some in the opposite direction. Since the same number of ships arrive at the cathodes and anodes in the same time, and exactly the same quantity of positive electricity is landed at the former as negative at the latter, the quantity of negative and positive electricity on the way will always be the same, *i.e.* no free electricity is found in the interior of the electrolyte. That the particles charged with negative and positive electricity pass without mutually neutralising each other is a difficulty which arises from our inadequate acquaintance with the nature of electricity. The same difficulty is met with in the case of a current flowing through metallic conductors, whether we assume the existence of one or two electric fluids.

Although electricity in the electrolytes only moves with the ions, the passage of the electricity from one molecule to another is not improbable. Numerous observations have shown that this transfer always takes place if several electrolytes following in direct contact with each other are introduced into the circuit. If the current is passed first through the solution of a barium salt and then of a sulphate, a precipitate of $BaSO_4$ is formed at the boundary of the two liquids,

$$Cl_2 \mid Ba + SO_4 \mid K_2 = Cl_2 \mid + BaSO_4 \mid + K_2,$$

so that the electricity carried by Ba is transferred to K_2 and carried on farther. We may, therefore, assume that such transfers occur, when they cannot be detected by the formation of a precipitate, or by a change of colour or other phenomena. It appears only to take place when the ion charged with electricity meets a molecule, decomposes it and combines with one portion, the other portion of the molecule transports the electricity which has been transferred to it. It is probable that this occurs frequently, perhaps it is of more frequent occurrence than it is for an electrical molecular fraction to pass by a complete molecule. At any rate, the distance which the electricity travels over in passing from one particle to another is very small compared with the distance it traverses in the company of the fractional molecule.

§ 304. The close connection between the conductivity of the electrolytes and the mobility of their molecules is clearly

demonstrated by the researches of G. Wiedemann,[1] O. Grotrian,[2] F. Kohlrausch,[3] and C. Stephan,[4] on the connection between the internal friction, or vicosity, of liquids and their electrolytic conductivity.

These experiments not only show that, as a rule, conductivity increases as the friction diminishes and as the mobility of the particles, or the fluidity increases, but they also prove that resistance to conductivity and resistance to friction are constants of the same order, which diminish in approximately the same ratio for an increase in temperature. The intimate connection of the conducting power with mobility is clearly shown by J. H. Long's[5] observation that the conductivity and rate of diffusion run parallel under similar external conditions—a substance which diffuses rapidly is, as a rule, a good conductor. In the following table the relative velocities of diffusion on page 289, column iv. under n, are compared with the results of Kohlrausch's determinations of the conducting powers λ, and the last column shows the ratio of n to λ.

		n	λ	$n : \lambda$
Potassium iodide . .	KJ	823	103	8·0
„ bromide . .	KBr	811	104	7·8
„ chloride . .	KCl	803	97	8·3
Ammonium chloride .	NH_4Cl	689	95	7·3
Sodium iodide . . .	NaJ	672	84	7·6
Ammonium bromide .	NH_4Br	629	103	6·1
Sodium chloride . .	NaCl	600	81	7·4
Lithium chloride . .	LiCl	541	70	7·7
Sodium bromide . .	NaBr	509	81	6·3
Ammonium nitrate . .	NH_4NO_3	680	93	7·3
Potassium nitrate . .	KNO_3	607	92	6·7
Sodium nitrate . .	$NaNO_3$	524	76	6·9
Lithium nitrate . .	$LiNO_3$	512	—	—

These numbers indicate that there is an approximate but not an exact ratio between n and λ. This is to be expected, as the conductivity depends on the mobility of the molecular fractions, and the velocity of diffusion on that of the undivided

[1] *Pogg. Ann.* 1856, xcix. 228.
[2] *Ibid.* 1876, clvii. 130; 1878, clx. 238; *Wied. Ann.* 1879, viii. 529.
[3] *Wied. Ann.* 1879, vi. 207. [4] *Ibid.* 1882, xvii. 673.
[5] Page 289, *loc. cit.*

molecules, which is approximately but not of necessity exactly proportional to the mean value of the mobility of both fractions. This close connection between velocity of diffusion and conducting power is evidence in favour of the hypothesis mentioned in § 301, that it is only the movement of the ions and not their separation which is the work of electricity.

§ 305. If a solution contains several electrolytes, each will act as a vehicle for the electricity, but it will be in proportion to the number of their equivalents present in the solution, and also, as far as the scanty material at present at hand permits us to judge, in proportion to their conductivity. Hittorf[1] found in electrolysing different mixed solutions of chloride and iodide of potassium, that the proportion between the two salts remains the same in all parts of the electrolyte; the decomposition of the salts must, therefore, be proportional to the equivalents present. In a solution containing equivalent quantities of the two salts, after the electrolysis, the two negative elements increased in the same proportion at the anode and decreased at the cathode. From a solution containing 3 KCl and 1 KI three equivalents of Cl were liberated to one of iodine. As both salts have approximately the same conducting power, these experiments show that the transference of the ions is proportional to the relative quantities of the two electrolytes in the solution.

The simultaneous electrolysis of salts of different conductivity in the same solution is by no means easy, as they either enter into double decomposition with each other or else form double salts, which behave electrolytically as simple compounds and only send one metal to the cathode, the other remaining a part of the anion. These contingencies can only be excluded with certainty in the case of salts containing one metal and two different acids, but here, as a rule, there is no great difference between the conducting power of the two bodies. It is, then, easy to understand why no exact experiments have been made in electrolysing mixtures of two good electrolytes of different conducting powers, and why no determinations have been made of the rates of migration, which

[1] *Pogg. Ann.* 1858. ciii. 47.

are essential for a correct knowledge of the nature of the process. It is very probable that in such a mixture both electrolytes receive the electricity in proportion to the number of their equivalents contained in the solution and are carried along with the velocity peculiar to their ions, so that each electrolyte is electrolysed in proportion to its conductivity and its electro-chemical mass, *i.e.* the electro-chemical equivalent contained in the unit of volume.

§ 306. The electrolytic change is frequently, if not always, disturbed and concealed to a greater or lesser extent by secondary actions which the free affinities of the ions exert on the different substances with which they come in contact, more especially on the electrodes, the electrolyte, the indifferent solvent, and on each other. These secondary actions have not of necessity any connection with the passage of electricity, and perhaps have nothing to do with it. They obey the ordinary law of chemical reactions and are merely characterised by the fact that the ions are in *statu nascendi*[1] and are consequently in a position to act very energetically. They lose this property as soon as several of them combine to form saturated molecules, *e.g.*

$$H + H = H_2.$$

This is not the place to describe the effects of these secondary actions, but it is worthy of note that they conceal the procedure of electrolysis to such an extent that gross errors can only be avoided by determining the rates of migration. Iodic acid, HIO_3, or $H_2I_2O_6$, offers one of the most remarkable instances of the case in point. In the electrolysis of this acid by a current of moderate strength, for each atom of silver precipitated and dissolved in the silver voltameter, $\frac{1}{5}$I at the cathode, and $\frac{1}{2}$O at the anode are simultaneously liberated. Hence it was formerly assumed that we were dealing with the anhydride of the acid I_2O_5 which is split up into $\overset{+}{I_2} \mid \overset{-}{O_5}$.

But Hittorf's[1] determination of the rate of migration proved that the electrolysis takes place according to the equa-

[1] *Pogg. Ann.* 1859, cvi. 401.

tion $\overset{+}{H_2} \mid I_2O_5, \overset{-}{O}$. The amount of iodine increases at the anode, the separation of iodine at the cathode is merely due to the secondary action of the hydrogen,

$$5H_2 + H_2I_2O_6 = I_2 + 6H_2O.$$

We are acquainted with numerous cases of the electrolysis of mixed or double salts, in which the cation precipitates from the solution surrounding the cathode, the more easily reducible metal belonging to the anion, or liberates hydrogen from water, or in which heavy metals are deposited by the secondary action of the hydrogen. In the technical application of electrotyping these processes are preferred because the metal deposited by the primary action is often crystalline, and that precipitated by the secondary action is more compact.

These secondary actions on the electrolytes may in many cases be avoided by making the electrodes very small, so that a large quantity of electricity flows through a relatively small layer of solution directly surrounding the electrode. As the current is very dense, more metal is deposited there than can be attacked by the quantity of liquid coming in contact with it. A portion of the deposit is thus protected from any secondary action until it is covered by a second quantity and preserved from further change. It is by this ingenious plan that Bunsen deposited metals which decompose water from aqueous solutions of their salts.

XVI.

THE STABILITY OF CHEMICAL COMPOUNDS.

§ 307. The various causes of chemical change have been discussed in the preceding chapters; this chapter will contain some reflections on the resistance which the different combinations of atoms oppose to the action of these forces. In speaking of the stability of chemical compounds, the term stability can only be employed in a relative sense, for compounds may offer a powerful resistance to one reagent and be easily attacked by another. It is, however, permissible to use the term almost in its absolute sense, because if a body offers a strong resistance to one force, it does not usually offer a very feeble resistance to another.

Compounds which are decomposed by a mechanical shock, or by the action of light, do not, as a rule, resist the action of heat and are easily decomposed by the affinities of other bodies; on the other hand, compounds capable of enduring a high temperature are generally stable towards other agents.

A comparison of the resistance which different chemical compounds oppose to the forces tending to accomplish their decomposition, shows that this power varies to an extraordinary extent. We find every imaginable intermediate stage exists between compounds on the one hand whose constituents are in such a state of unstable equilibrium that they are decomposed by the slightest shock, and, on the other hand, bodies which can only be decomposed with the greatest difficulty. Stability varies within the widest limits.

This great difference depends on widely different causes, but ultimately on the nature, number, and mode of linking of the atoms forming the molecule, for it is on these three points that all those chemical and physical properties of the body depend, which determine its stability. It is rarely possible to

determine exactly the separate influence which each of these three conditions exerts on the stability of a body. As it is the material nature of a body which determines the number and the arrangement of the atoms in the molecule, this is the ultimate cause on which the stability of a chemical compound depends.

It is the problem of a doctrine of comparative affinities to represent the relation between the nature of the elements and the stability of chemical compounds, and the reactions of which they are capable or incapable, and to discover the laws which govern this connection. But although an enormous number of observations have been made on the reactions of chemical compounds, very few have been made from the comparative point of view. It has been done now and again for small groups of analogous compounds, but it has only been done on the large scale when it was of importance in the analysis or synthesis of compounds. Our handbooks and treatises are chiefly of the systematic descriptive class. No attempt has yet been made at a doctrine of comparative affinity which should bear the same relation to descriptive chemistry that comparative anatomy and physiology do to systematic zoology. Such a work would excite more active interest than the mere description of bodies.

§ 308. The influence which the material nature of an element exerts on the stability of its compounds obviously depends on the nature of the other elements it is combined with, because the strength of its affinity varies with different elements. As a rule the affinity of two elements increases, the further apart they are in the electro-chemical tension series; hence compounds of strongly positive and strongly negative elements are very stable. But we are not justified in saying that the greater the contrast the more stable the compound will be. Generally, compounds of adjacent elements (*i.e.* in the tension series) have little stability, but there are many exceptions; the compound may be very stable if the atoms are perfectly similar, as is seen in the case of the molecules of many elements which are composed of more than one atom.

When the atoms contained in the molecule of an element firmly adhere together, that element will not, in the isolated

state, readily enter into combination, and its molecules must be strongly heated to bring this act of combination about. A comparison of the different elements shows that it is the molecules of the most strongly positive or negative elements which most readily decompose. Cl_2, Br_2, I_2, and probably F_2, and also the compounds of these elements with each other, ICl, IBr and ICl_3, head the list in this respect. If the molecules of the metals of the alkalis and the alkaline earths are composed of more than one atom and not of single atoms, they will follow next in order (with the exception of Mg). Of the negative elements, oxygen, sulphur and selenium are less ready to form compounds than the halogens. In the case of S, Se and partly in the case of O, this may be due to the fact that their affinities are weaker; without doubt the greater stability of their molecules is caused by this fact, especially in the case of oxygen, whose power of entering into combination at a higher temperature or when its atoms are in a loose state of combination, as in ozone, is equal to that of chlorine.

At low temperatures, the less negative non-metallic elements, especially carbon and nitrogen, have a very slight tendency to enter into combination, but at high temperatures they unite with many other elements to form very stable compounds. We may therefore conclude that their atoms have a great tendency to unite firmly together.[1] In the case of carbon this is proved by the numerous organic compounds. At the ordinary temperature it is scarcely possible to sunder the atoms of nitrogen from their molecular chain N_2; it is only attacked by ozone. Under the influence of the electric spark nitrogen unites with hydrogen to form ammonia, and at a white heat it combines with almost all the elements which are found in the vicinity of nitrogen, in the periodic system of elements (§ 61), especially with boron, silicon, titanium, zirconium, vanadium and chromium, perhaps also niobium and molybdenum. Nitrogen also unites with magnesium and in small quantities with aluminium. Even at a high temperature nitrogen only combines with carbon to form cyanogen, in the presence of hydrogen, or a metal or some of the so-called semi-metals. The presence of titanium is especially favour-

[1] For the physical proof *vide* E. Wiedemann, *Wied. Ann.* 1883, xviii. 509.

able to the reaction. Now the compounds derived from free nitrogen at a red heat are very stable; we may therefore conclude that the atoms in these compounds as well as in free nitrogen are united together by a powerful affinity. It is remarkable that almost all the elements (except oxygen) which unite directly with nitrogen are infusible and non-volatile, viz. B, C, Si, Ti, Zr, V, Cr.

Little definite is known regarding the stability of the molecules of most of the metals and semi-metals; but we may assume that it is not very great, as some metals at least split up into single atoms when they are volatilised, and most of them unite readily with chlorine and generally with oxygen. Among the platinum metals, more especially in osmium and iridium and their compounds, we find bodies whose stability resembles that of free nitrogen and the metallic nitrides.

§ 309. As a general rule to which there are some exceptions, compounds of different elements are less stable when the elements bear a close resemblance to each other. Metallic alloys are generally attacked by reagents without difficulty. In the same way compounds composed entirely of negative elements are as a rule easily decomposed, *e.g.* the compounds which the halogens form with each other and with oxygen, the oxides of other negative elements, such as sulphur, selenium, tellurium, nitrogen, arsenic, &c. On the other hand, the negative element phosphorus is characterised by a very great affinity for oxygen which exceeds that of many positive elements. The non-metals boron, silicon, and the semi-metals molybdenum, vanadium, tungsten, tantalum, titanium, &c., combine more firmly with oxygen and often with nitrogen than many metallic elements of positive character. The most positive of all the alkali metals are more easily separated from oxygen than the less positive earthy metals.

The most negative of the malleable metals, the noble metals platinum, palladium, rhodium (and also the brittle metal iridium), gold, silver, mercury, form with oxygen compounds of little stability, as might be expected from their electrical position. But in the electric tension series, carbon, which is characterised by its great affinity for oxygen, comes next to platinum. Chlorine, bromine and iodine do not unite

directly with carbon, but the noble metals are readily attacked by them. These compounds differ greatly in their stability; silver and mercury form very stable compounds with chlorine, but the chlorides of gold, platinum, and allied metals easily part with their chlorine.

The exceptions to the above rule are so numerous that its validity is doubtful. It is at any rate clear that the stability of compounds is not solely determined by the electrochemical properties of the elements. So little is known of the real nature of what is termed electrochemical contrast, that we are not in a position to discuss in detail its relation to the stability of compounds.

§ 310. The stability of a compound is not only intimately connected with the electrochemical properties of its elements but also with their position in the series of atomic weights. The behaviour of the elements with oxygen, the stability of their oxides, can be represented in connection with the curve of atomic volumes (§ 63). All the elements occupying positions between each maximum atomic volume, to a point a little beyond the next minimum, combine with oxygen, forming very stable compounds; their oxides can only be reduced with difficulty. The elements from this point to the next maximum form easily reducible oxides, as the following table shows.

Difficultly							Moderately			Easily reducible						
I.	II.	III.	IV.	V.	VI.	VII.	H			I.	II.	III.	IV.	V.	VI.	VII.
Li,	Be,	B,	C,				VIII.		VIII.					N,	O,	F,
Na,	Mg,	Al,	Si,	P,											S,	Cl,
K	Ca,	Sc,	Ti,	V,	Cr,	Mn,	Fe,	Co,	Ni,			Cu,	Zn,	Ga,	—	As,	Se,	Br,
Rb,	Sr,	Y,	Zr,	Nb,	Mo,	—		Ru,	Rh,	Pd,	Ag,	Cd,	In,	Sn,	Sb,	Te,	I,	
Cs,	Ba,	La,	Ce,	Di,														
		Yb,		Ta,	W,			Os,	Ir,	Pt,	Au,	Hg,	Tl,	Pb,	Bi,			
			Th,		U,													

The boundary does not always lie in the same group. Some elements occupy an intermediate position, such as the iron group and hydrogen, which probably occupies an analogous position near a minimum.

Similar groups are obtained by classing together the elements which have a greater affinity for chlorine than for oxygen, whose oxides are decomposed by hydrochloric acid, and arranging together the elements whose chlorides are partly or completely decomposed by water, elements having a greater affinity for oxygen than chlorine.

The former are found in the atomic volume table near the maximum and minimum, the latter occupy the ascending and descending portions of the curves between these two points.

Numerous other examples could be given, to exhibit the connection between the stability of compounds and the nature of the atoms contained in them.

§ 311. In the separate families and groups there is a regular variation of the affinity and, at the same time, of the stability of the compounds with the atomic weight, but not always in the same direction.

In the groups of the most positive elements, the alkalis and alkaline earths on the one hand, and in those of the most negative elements, the halogens and the oxygen group on the other, the stability of the compounds with negative elements increases with the atomic weight and the stability of the compounds with positive elements diminishes. In the group of the heavy metals this behaviour is generally reversed. A smaller atomic weight corresponds to a greater affinity for negative elements and consequently to increased stability of the compounds. This is clearly exhibited in the following families—Cu, Ag, Au: Zn, Cd, Hg: Ga, In, Tl, Sn, Pb. The group embracing P, As, Sb, Bi behaves in the same way, but the first member of the group, nitrogen, is far behind phosphorus in the stability of its compounds with negative elements. In group VIII. the compounds of the elements with the lower atomic weights Fe, Co, Ni, are much more stable than those of the elements with high atomic weights, the platinum metals.

In many groups the distinction is not clearly defined; our knowledge of others is not complete enough for them to be clearly indicated. Even in the examples we have mentioned there are many exceptions. It will be the problem of the doctrine of comparative affinity to investigate these cases more thoroughly and to determine their connection with the nature of the elements.

§ 312. The number of atoms contained in a molecule also exerts an influence on the stability of the compound, an influence which is especially marked in the case of polyvalent elements. If a polyvalent element forms several compounds

with a mono- or di-valent element, then the higher compounds of the series are apt to lose some of these mono- or di-valent atoms, under certain conditions, and pass into lower members of the series. Under the influence of heat many chlorides and oxides lose a portion of their chlorine or oxygen, viz. the higher chlorides of copper, gold, thallium, platinum, phosphorus, antimony, vanadium, molybdenum, tungsten, &c. and the highest oxides of nitrogen, arsenic, antimony, chromium, manganese, &c. But it often happens that the lower oxide or chloride which is more stable under the action of heat is less stable as regards some other agent than the higher chloride; *e.g.* tungsten pentachloride is less stable than the hexachloride towards moist air; nitrites which are obtained by the action of heat on nitrates are less stable towards chemical reagents than the nitrates; and sulphites are less stable than sulphates, &c. This is probably due to the fact that the loss of the atoms which were required for the complete saturation of the compound has materially affected the equilibrium of the molecule and has exposed weak points to the affinities of other atoms, which were completely protected in the saturated compound by the atoms which have been removed from it.

§ 313. The influence of atomic linking on the stability of compounds is particularly conspicuous in those bodies which contain the same number and same description of elements, and yet possess different properties. This occurs in the case of allotropic modifications or of isomerism. Such instances are by no means rare in Inorganic Chemistry; nevertheless hardly anything is known about the difference in the atomic linking of the isomeric or allotropic compounds. It is different in Organic Chemistry, where a very large number of cases of isomerism can be explained by the difference in their atomic linking, which has been accurately ascertained. The time has arrived when it is possible to establish a doctrine of the equilibrium of the atoms in organic compounds, dealing with their destructibility and their decomposition. It must determine for each separate kind of atoms or groups of atoms occurring in organic compounds, the manner in which the force which holds them in combination depends on the atomic linking. Many observations have been made which might

serve as a basis for such a comparison. Apart from the fact that our space would not suffice for such an extensive project, we willingly leave it to those chemists who have actually cultivated this branch of research.

It will suffice to add a few additional examples to those previously mentioned in § 103. The aromatic compounds furnish us with the most striking examples, which not only contain the same atoms but also the same groups of atoms combined in different sequence. For example, there are three isomeric dimethylbenzenes $C_6H_4Me_2$; metaxylene is not attacked by dilute nitric acid, but ortho- and para-xylenes are oxidised to monobasic acids of the composition MeC_6H_4COOH, ortho- and para-toluic acids; chromic acid oxidises meta- and para-xylene to the dibasic acids $C_6H_4(COOH)_2$ isophthalic and terephthalic acids, but it converts orthoxylene into water and carbon dioxide. Metahydroxy-benzoic acid resists the action of heat and of acids better than the isomeric salicylic and parahydroxy-benzoic acids. Phthalic acid is decomposed by heat into the anhydride and water, but its isomerides sublime without decomposition. These differences in stability can only be due to the atomic linking, and this is true of thousands of other similar cases.

§ 314. There are numerous cases in which the substitution of one or more atoms for others, without changing the atomic linking, has increased or diminished the stability of the whole compound. The fact frequently observed that an unstable acid is converted into a stable salt by the substitution of a metal for hydrogen belongs to this category. This phenomenon is observed in the oxy-acids of chlorine and their analogues, in most of the acids of sulphur, especially hyposulphurous acid, also in nitrous, permanganic acids, &c. Many acids which easily decompose into the anhydride and water form very stable salts, *e.g.* carbonic, silicic, sulphurous, arsenious, chromic, &c.

The nature of the metal replacing the hydrogen is by no means unimportant for the stability of the compound, but the laws governing the relation between the nature of the metals and the stability of the salts have not yet been ascertained. Certainly the difficultly reducible metals of the alkalis and alkaline earths import great stability to the salts.

But certain of the more or less easily reducible heavy

metals also have this property, indeed the salt of the more easily reducible metal is often the more stable of the two, *e.g.* the sulphate and nitrate of silver are less easily decomposed by heat than the corresponding salts of copper, zinc, and even magnesium. Analogous compounds of closely-related metals often exhibit a striking difference in their resistance to heat, *e.g.* cobalt sulphate is much more stable than any of the isomorphous sulphates of nickel, iron, copper, zinc, and even magnesium. Nothing is known of the cause of this difference in stability.

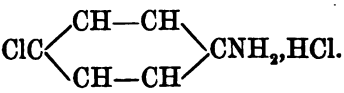
Many salts are more stable after they have united with other salts to form double salts, *e.g.* the chlorides of platinum, gold and of many other metals and semimetals. Some examples have already been given in § 103, of the alteration in the stability of organic compounds by substitution. These have illustrated the remarkable fact that the influence of the substitution is by no means confined to the atoms, which are directly united to the substituted atom. The conversion of $-CH_2OH$ to $-COOH$ is facilitated by replacing the hydroxyl hydrogen by a metal, but it is retarded by replacing the hydroxyl by chlorine; the nitration or chlorination of the benzene nucleus in phenol increases the force with which the oxygen combines with a metallic atom which has been substituted for the hydrogen in hydroxyl. Perhaps the unstable carbon tetra-iodide CI_4 offers the best example. It easily exchanges its four iodine atoms, for oyxgen, but if one hydrogen atom is substituted for one of the four iodine atoms and the tetra-iodide is converted into iodoform CHI_3, then these three atoms of iodine are much more firmly attached to the carbon atom than the four iodine atoms in the tetra-iodide.

The influence of the substitution on the stability of the compounds often extends over many members of the chain. The stability of the salts of the amines diminishes with the successive substitution of negative elements for hydrogen in the hydrocarbon radicle attached to the carbon.

Aniline is a base of feeble avidity according to Menschutkin[1] $\frac{1}{x} = 0$. It forms stable salts, *e.g.* aniline hydrochloride,

[1] *Compt. rend.* 1883, xcvi. 256. Menschutkin believes that his experiments are not in unison with the theory of Guldberg and Waage. L. Meyer is of

$Ph.NH_2HCl$. A single chlorine atom in the benzene nucleus appreciably dimininishes its stability, even if it is in the para position which is the most distant from the nitrogen,



Here the action of the chlorine attached to one carbon atom extends through three others to the nitrogen atom and enfeebles the basicity. A second chlorine atom, at any point in the benzene nucleus, diminishes the attraction between the amide $-NH_2$ and the acid to such an extent that it ceases to form salts. The introduction of $2CH_3$ for H_2 in NH_2 enables it once more to unite with acids. Similar effects increasing or destroying the stability of compounds are the rule, not the exception.

§ 315. When we speak of the stability of chemical compounds, the term stability is merely relative, as this property varies widely with different forces. It is the result of several different causes some of which tend to bring about the decomposition of the compound and others to oppose it. In order to separate these different causes and their effects it is necessary to make a thoroughgoing comparison of the behaviour of the different categories of compounds, based as far as possible on quantitative measurements. By the comparison of analogous groups of compounds, and the determination of their points of resemblance and difference, material will be collected for a doctrine of comparative affinity which will trace the behaviour of compounds, the conditions of their formation and decomposition, to the properties of the atoms as the ultimate cause. As our knowledge progresses in this direction, chemistry will gradually lose the character of a descriptive and acquire that of a speculative science. Not that there is any lack of theorising in chemistry, but that the speculations will gain a firmer basis, and we shall be in a better position to predict with a greater amount of certainty the results of an experiment.

opinion that this is not the case, for as x^2 may have any positive value, x^2 may $= \infty$, and consequently $\frac{1}{x} = 0$.

XVII.

CONCLUSION.

The necessity of hypotheses and theories as aids to experiment and observation was recognised by Bacon more than two-hundred years ago in the Aphorisms 'de interpretatione naturæ' of his 'Novum Organum.' 'Nec manus nuda, nec intellectus sibi permissus multum valet: instrumentis et auxiliis res perficitur, quibus opus est non minus ad intellectum quam ad manum.' Hypotheses and theories are the aids and instruments of thought, but chemists have not at all times recognised their necessity. On the contrary, the history of chemistry shows that periods in which theoretical speculations were too highly esteemed have repeatedly alternated with periods in which these speculations were neglected or treated with scanty respect.

Bacon himself says of the chemical theories of his contemporaries: 'Chymicorum autem genus ex paucis experimentis fornacis philosophiam constituerunt phantasticam et ad pauca spectantem,'[1] and this criticism has often applied in later days.

Even at the present time, hypotheses are only too frequently based on unreliable or incomplete observations, which appear to give a plausible explanation for a very narrow circle of phenomena, without excluding other explanations of the same phenomena. They are frequently incapable of any general application. It is obvious that such attempts at theories, which often require more arbitrary assumptions than the number of facts they are intended to explain, are not destined to last long. It is clear that a preponderance of such theories in chemistry tends to diminish for a time the importance attached to theoretical speculations, and consequently

[1] *Nov. Org.* I., Aph. liv.

there was at one time a desire in discussing chemical facts to avoid even well-founded theories as long as it was possible to do without them. Indeed, it was believed that the rich empirical material could be systematically arranged without the aid of theory.

The two hypotheses on which the modern development of theoretical chemistry is primarily based, viz. Avogadro's hypothesis on the molecular constitution of gases and that of Dulong and Petit on the capacity for heat of the atoms, have both experienced this fate.

In the case of Dulong and Petit, it was not altogether undeserved, as the erroneous conclusions drawn from their hypothesis, combined with incorrect and unreliable observations, more than once threatened to upset the results of other and better observations, and even misrepresented well-known facts and prevented a correct insight into their mutual connection being attained. But after the validity of this hypothesis was confined within its true limits and after almost all the deductions derived from it were brought into complete agreement with other results of investigation, a considerable time elapsed before it met with general acceptance. Although at the present time no open opposition is offered to this hypothesis, there are still some noted chemists who make use of other atomic weights of the elements than those required by this undoubtedly correct hypothesis.

Avogadro's hypothesis received very similar treatment, although the only objection brought against it is that mentioned in §§ 28 to 34. It was its misfortune that even at the very beginning Avogadro's molecules were straight away identified with Dalton's atoms, although it is impossible for any attentive reader not to see that Dalton's atoms could only be fractions of Avogadro's molecules. Twenty years ago (1864), when this book first appeared, neither of these hypotheses could be said to be universally acknowledged. Many chemists neither denied nor accepted but simply ignored them. As a rule, text-books and lecturers only availed themselves of a small portion of their results. This has been entirely changed by the subsequent development of Organic Chemistry. The hypotheses of Avogadro and of Dulong and

Petit are universally acknowledged to be the bases of the determinations of atomic and molecular weights. Gmelin's so called equivalent weights have almost disappeared from our literature, and Berzelius's numbers justified by these hypotheses have again gained the ascendency.

This opposition to the introduction and adoption of well-founded theoretical considerations forms a sharp contrast to the stubbornness and tenacity with which hypotheses and theories once introduced into the science are retained, even when they have grown untenable, by the most cautious and experienced chemists. The belief in the existence of phlogiston for a long time prevented, in an incomprehensible way, highly gifted chemists from acknowledging the correctness of Lavoisier's conclusions. Berthollet, blinded by his love for his theory of the action of mass, raised the strongest opposition to the laws of stochiometry. Berzelius pertinaciously disputed Davy's theory of the elementary nature of chlorine, because it revolutionised the system of chemistry,[1] and did not conform with his electrochemical theory.[2] For the same or similar reasons he denied the theory of substitution maintained by Dumas, Laurent and others, even when almost all the other chemists had acknowledged it, and he declared with many other authorities that the only correct theory of the constitution of chemical compounds[3] is the so-called dualistic theory, in opposition to the unitary or type theory, maintained by Laurent, Gerhardt, &c. The history of chemistry offers numerous examples of this kind.

On the other hand, no hypothesis has been adopted with less hesitation in chemistry than Dalton's Atomic Theory. It is true also that no other theory penetrates so deeply into the nature of chemical changes and no other theory can yield such overwhelming confirmation of its truth. But even sharply criticised hypotheses have often gained a rapid acceptance. In 1864 the theory of atomic linking was only in the first stage of its development, and its validity was disputed by many chemists of high standing. Even many of its followers were ignorant of the true signification which the for-

[1] *Gilb. Ann.* 1812, xlii. 288. [2] *Ibid.* 1815, l. 367, 410, 445.
[3] *Vide* § 122.

nuke of the typical system concealed. It soon met with approbation, and has proved in the most brilliant manner its capability for further development.

The atomic theory succeeded not only in regarding the quantitative composition of compounds from one general point of view, but it succeeded in correctly predicting the composition of innumerable compounds, and the theory of atomic linking not only explained the large number of known cases of isomerism, but it led to the discernment of a much larger number and to the discovery of a new and peculiar class of compounds.

It is only natural that the weight and authority of hypotheses and theories in chemistry should be increased by such results as these. The hesitation which formerly prevailed in making use of theories gave way to the custom of placing theoretical views as much as possible in the foreground and only employing the results of observations to confirm the speculations. Hypotheses and theories now occupy a far higher position than they did at the time when this book, which deals only with theories, first appeared.

An intelligent critic will hardly seek to account for this real or apparent contradiction, between the alternately high and low estimation in which hypotheses and theories have been held, by an uncertainty in opinion. In a science which embraces such a large number of talented followers, it is impossible for any erroneous notions to prevail as to the value or worthlessness of hypotheses and theories. The vicissitudes in the position which theories hold in chemistry are essential results of the condition of chemistry itself at the time.

The value of hypotheses [1] is essentially twofold in nature. In the first place it depends on the purely practical advantage which it brings. The progress of the science depends on the establishment, confirmation or destruction of hypotheses by experiment. This use of hypotheses has been witnessed in chemistry since its very beginning to such an extent that when the value of hypotheses is mentioned in chemical treatises, it is only this advantage which is usually cited. In

[1] *Vide* Berthollet's *Statique Chimique*, p. 4–10; also Marignac's 'Report on Maumené's Theory of Affinities,' *Bibl. Univ. Arch.* Jan. 23, 1865, p. 76.

fact this in itself is great enough to justify the use of hypotheses.

But the value and the use of hypotheses are not merely confined to the inducement they offer to the chemist to undertake new investigations with the object of testing, proving, or disproving their validity. The simple knowledge of things as they are or appear to be does not satisfy the inquiring spirit of man. He endeavours to fathom the ultimate cause of things, of all changes and of all actions. This aim will doubtless never be attained. Our ideas can never be identical with the real nature of things, but they can more and more closely approximate to them, as shadows more and more sharply reproduce the shape of an object. But, in order that our ideas may more and more closely resemble the true nature of things, we must first of all set up hypotheses, and logically develop the results of these hypotheses, with or without the aid of mathematics, into a theory, and compare the results of this development with phenomena accessible to our powers of observation. The closer the agreement between theory and observation, the greater will be the probability that our hypothesis gives an approximately correct, if not absolutely true, representation of the nature of the phenomena. This state of probability is the highest aim which the natural sciences can hope to attain. The increasing probability may grow nearer and nearer to certainty, but it can never be transformed into absolute infallibility.

Here lies the danger in the use of theories and hypotheses. It proceeds from the difficulty of judging the degree of probability and of definitely deciding between probability and certainty. In the case of such a young science as the exact chemistry it is often difficult to separate those parts of the theory which are only the abstract expression of observed facts, and which therefore possess the highest degree of certainty which the perceptions of the senses can possibly possess, from the really hypothetical assumptions which are introduced into our speculations. If no distinction is made between these two classes of hypotheses, then facts and hypotheses grow together in such rank confusion that it becomes difficult to dispense with hypotheses which have become very improbable.

It is then easy to retain them too long and when finally such a hypothesis is abandoned as quite untenable, it may easily shake the science to its very foundations. Chemistry has already experienced no slight number of these violent upheavals, from the time of the overthrow of the phlogistic theory to the period when the systematic classification by series and types was accomplished.

If chemistry is to be spared from fresh disturbing catastrophies it is above all things necessary to arrive at a correct valuation of the hypotheses and theories which we hope will soon be the common property of all investigators.

Just as we have happily overcome the false depreciation of hypotheses and theories and the exaggerated fear of their pernicious influence, we shall also succeed in banishing the opposite extreme from chemistry, viz. dogmatising, frivolously proposing and overestimating the value of hypothetical assumptions. The chemical journals of our days are rich in treatises which begin with detailed speculations prompted by theory but not confirmed by observation, and end with another and different theoretical representation which is apparently adapted to the unexpected results of observation. Then *a posteriori* the observations very often appear as a confirmation of the theory which was arrived at *a priori* from quite different predictions. This want of agreement between speculation and experiment is particularly noticeable in attempts to prepare compounds known to be theoretically possible, not in the existence or non-existence of these compounds. Where theory indicates the possibility of a definite compound, it is generally possible to prepare it, but the first attempt seldom succeeds. The methods which according to theory appear to offer the best promise of success often lead to no result or to an unexpected one; frequently an experiment often repeated under different conditions yields the desired result, but very often the compound which has long been sought for in vain will be accidentally discovered by a method which was not expected to yield it. It has not seldom happened, even in recent times, that whole classes of compounds have been discovered whose existence was not foreseen by the theory of atomic linking.

This undeniable source of weakness exposes the theory to

a danger which must not be underestimated. It is the tendency, especially in many new text books, to treat chemistry as a deductive science. No doubt chemical compounds and their relations to each other can be more systematically represented and more easily grasped, if we regard them from a common standpoint as the necessary results of a few general laws. We may acknowledge that at the present time the theory of the chemical equivalence of the elements and the law of atomic linking have proved themselves qualified to be regarded as universally valid laws. They have averted the threatened confusion of Inorganic Chemistry, brought about by the overthrow of the electrochemical system; they have given a systematic arrangement to Organic Chemistry, which the electrochemical theory was quite incapable of doing. But in their time the phlogistic theory and the electrochemical theory rendered the same service, for they created a new systematic order in chemistry, and brought about the discovery and the prediction of a multitude of phenomena. Nevertheless they have fallen, and, although most of the good in them has been retained, still many a correct notion has been buried with the untenable views of these theories, to be rediscovered and to receive its proper recognition after an interval of many years. The fate of our present theories can hardly be different. As was the case with the older ones, a portion of our present theories will be retained, but another portion, which even now appears to be tottering, will after a time be found to be untenable. If the next transition in our hypotheses is to avoid the strife and confusion which the change from the phlogistic to the antiphlogistic, or from the dualistic to the unitary theories brought about, we must take care to keep separate in our present theories everything which is a direct expression of observed facts, on the one hand, from what, on the other hand, has been added to our observations by theories and hypotheses, so that we may always know what has an empirical and what has only a hypothetical basis in our theories. It is not the promulgation and the defence of hypotheses and theories which create violent and bitter discussions, but it is the confusion of hypothesis with unassailable truth. If the hypothesis of phlogiston and the dualistic theory had not acquired the form and im-

portance of infallible dogmas, the fact would now be more frequently recognised that they were in their time useful but unproved hypotheses, and their transformation would hardly have shaken the whole science to its very foundations and have retarded the progress of the science to the extent which it did.

There is no fear that those chemists living who witnessed the struggle between the dualistic and the unitary theories, between electrochemical theories and types and atomic linking, will ever involve themselves in a similar struggle. But a new generation is now at work side by side with the older chemists in the same field, for whom the dualistic system has scarcely more than an historical signification, and on whom the experiences of the last great struggle cannot have made such a deep and lasting impression as to produce a perpetual remembrance of the experiences. In fact, the current chemical literature shows that the young generation is much more inclined than the old to treat chemistry dogmatically, especially the doctrines of the chemical equivalence of the elements and the linking of atoms.

Assertions based on very hollow hypotheses are at the present time stated with a degree of positiveness, and are defended with an amount of stubbornness, which is not inferior to that exhibited by the supporters of the phlogistic theory, nor to the bitterly blamed dogmatic infallibility of the electrochemical dualistic system, although these new theories do not possess the general utility and universal applicability which both the older theories appeared to possess when at the height of their power.

The impartial observer easily recognises that the atomic theory is the only chemical theory which enters deeply into the nature of chemical phenomena, in the same way that the undulation theory penetrates into the nature of light and heat. Each chemical theory deals with the atoms and their mutual relations superficially, and merely from one point of view. Lavoisier's chemistry was onesided, the electrochemical dualistic theory was onesided, and so also are the substitution theories of Dumas and Laurent, and Gerhardt's type theory. The theories of atomic linking and of the chemical

valence of the elements are both onesided. When one theory displaced another, this was, as a rule, not so much due to the strength of the victor, as to the weakness and untenability of the views of the vanquished. Each system which acquired ascendency maintained it so long as it appeared capable of offering a satisfactory explanation of the most important and most striking phenomena. It lost it when a large number of observations were made which it could not satisfactorily explain. This exchange of one-sided systems will probably be often repeated before we succeed in finding a hypothesis which enters more deeply into the nature of chemical atoms, and from which a general theory can be developed, which will embrace all chemical phenomena.

Each new transformation leaves behind it a larger treasure of valuable results, and leaves the nucleus of the science less dependent on the dominant theories.

The present state of the science is well fitted to show the state of independence we have attained. The rich mass of material can be arranged and treated from the most widely different points of view. The arrangement is essentially the same, whatever may be the difference in the fundamental opinions of the authors; for it is determined by the facts themselves, it no longer requires the support of theory.

As the science advances the injurious influences of hypotheses and theories can be more easily avoided. We can guard against them more completely and with greater certainty if we carefully avoid mistaking hypotheses, be they ever so probable, for irresistible truths. On the other hand, we must carefully avoid depreciating hypotheses and theories. Just as caution and deliberation are strongly to be recommended in bringing forward hypotheses and introducing them into the science, on the other hand, no hypothesis which has shown itself of general application should be set aside as soon as one or two facts are discovered which it does not appear capable of explaining. We should rather, in the first place, attempt to alter and improve it, and even if this is not at once successful, a disputed hypothesis capable of improvement may for a time be of service to the science. But when it is proved that the deductions from a theory are directly

opposed to the results of observation, then the hypothesis must be at once abandoned and replaced by one which conforms more closely with the facts. Hypotheses cannot be dispensed with; they are the necessary implements of chemical theory and of every other theory. An exact knowledge of the implements, their capabilities, strength, and weaknesses is the first requirement for the safe and successful completion of the structure.

The more chemists accustom themselves to the correct use of hypotheses, the more unhesitatingly will new ones be introduced; and this is the more necessary as the science becomes less one-sided. This necessity has already been pointed out in the first edition of this work.[1]

'It will be necessary in the immediate future to introduce some few new hypotheses. It appears that many of the fields of molecular physics, which are closely allied to, and are in the almost exclusive possession of chemistry, cannot be successfully cultivated at present, especially the theoretical hypotheses and speculations introduced and developed by Clausius, which explain the different conditions and forms of matter by the assumption of different forms of motion of the corporeal molecules.

'These views, proceeding from the fundamental principles of mechanics and especially the mechanical theory of heat, alone appear capable of penetrating into the influence which the chemical nature of bodies, the atomic constitution of their molecules, exert on the changes of the states of aggregation, *e.g.* fusion and solidification, evaporation and condensation, on vapour pressure and on the phenomena of diffusion, absorption, solution, crystallisation, imbibition, endosmose, and all similar processes. A successful theoretical investigation of electrolysis and of the whole field of electrochemistry appears to be only accessible from this side.[2] Perhaps these views will soon be indispensable in considering all purely chemical reactions, chemical decomposition and chemical combination, although very similar views have independently

[1] Page 144.

[2] *Vide*, 'Ueber die Elektricitätsleitung in Elektrolyten,' by R. Clausius, *Pogg. Ann.* 1857, ci. 338.

sprung up from the consideration of purely chemical reactions.'[1]

This prediction has been fulfilled. The kinetic theories of the states of aggregation are universally accepted; they have proved to be exceedingly fertile and have permitted us to gain an insight into the nature of the small particles of matter, the molecules, which was formerly hardly anticipated. They have already been discussed in the previous editions. The fourth and fifth editions contain the kinetic theory of electrolysis by Clausius, and also Guldberg and Waage's kinetic theory of the action of mass, which is developed from the views of Clausius and Williamson.

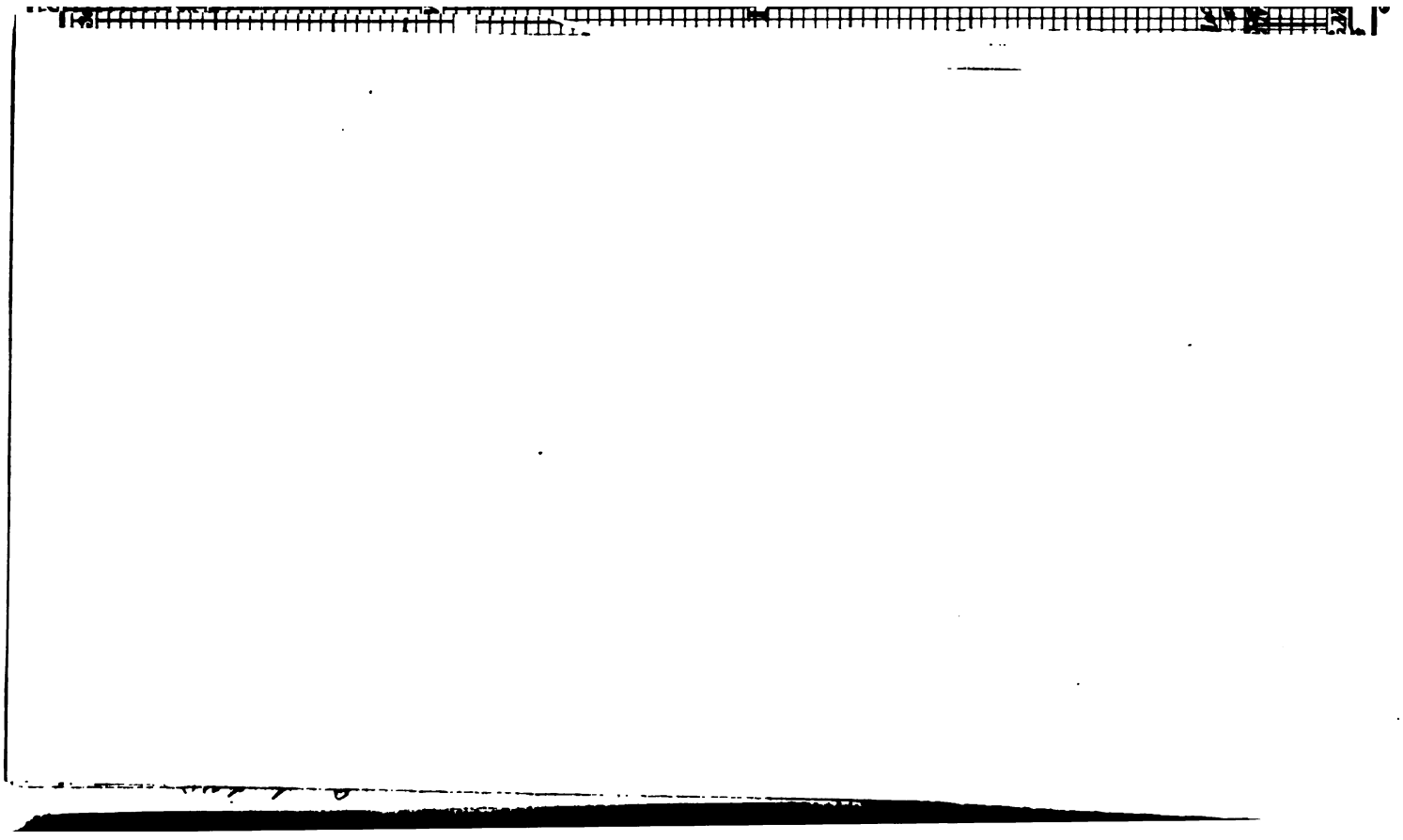
On the other hand, we must still lament (section XII) the absence of kinetic speculation on the thermic changes accompanying chemical change, and it has been shown that in this important branch of science matters of fact run the danger of being obscured and misrepresented, owing to the survival of antiquated theoretical notions. This may account for the fact that another prediction in the first edition is still waiting for fulfilment, viz.—

'It is by no means improbable that the contemplation of the movements of the smallest material particles will be permitted to exert a much deeper influence on chemical theories. The gravitation of the heavenly bodies has been explained, without the difficult assumption of an attraction working at a distance through space, by means of the single hypothesis of a medium, ether, pervading the universe, the particles of which are imbued with a very active motion.[2] We may perhaps succeed in dispensing with other forces of attraction, such as affinity, cohesion, &c., which are now generally assumed to exist, and be able to show all the phenomena ascribed to these forces, as the necessary results of the movements proceeding from the smallest particles of matter, in the forms of light, heat, &c.'[3]

[1] *Vide*, 'The Theory of Etherification,' by A. Williamson, *Lieb. Ann.* 1851, lxxvii. 37.

[2] Le Sage, *Deux Traités de Physique mécanique*, publiés par Pierre Prévost, Genève et Paris, 1818. P. Prévost, *De l'origine des forces magnétiques*, 1788, chap. 2, 'Principes physiques.'

[3] Such an attempt was made by Le Sage, *Essai de Chimie Mécanique*,



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